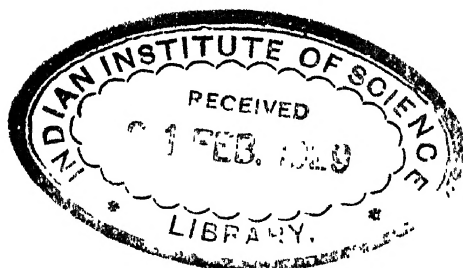# THE VISCOSITY OF LIQUIDS

THE VISCOSITY
OF LIQUIDS

BY

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PREFACE

THE author has found in the teaching of Colloid Chemistry, more particularly in the laboratory, that the subject of Viscosity is one which seems to present difficulties to the majority of students. The more enterprising among them have often asked him to "recommend a book," but he has generally found it necessary to refer them to text-books or hand-books of physics for some points, and to original papers for others.

In the present work the author has attempted to present, in a moderate compass and without excessive mathematical apparatus, as much of this scattered information as will give the reader a grasp of the fundamental principles and a general view of the subject. The task of selection from the enormous mass of material available has been difficult, but the author has had the advantage of being able to include some investigations of great importance, like those of Bridgman, which have not so far found their way into any text-books. He has also thought it advisable to devote a chapter of some length to the viscosity of colloidal solutions, a subject of peculiar difficulty calling for a great deal of further research, which a summary of the present position may perhaps help to stimulate.

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VISCOSITY OF LIQUIDS

CHAPTER I

FUNDAMENTAL CONCEPTS AND HISTORICAL DEVELOPMENT

IF portions of a mass of liquid are caused to move relatively to one another, the motion gradually subsides unless sustained by external forces; conversely, if a portion of a mass of liquid is kept moving, the motion gradually communicates itself to the rest of the liquid. These effects, which are matters of immediate observation, were ascribed by Newton to a "defectus lubricitatis," *i.e.* a "lack of slipperiness" between the particles of the liquid, which may be fairly interpreted to mean a property resembling friction between solid surfaces, and Newton, in fact, uses the term "attritus," *i.e.* friction, several times in the course of his deduction. The terms "internal friction" and "viscosity" have been used indifferently to describe this property of liquids; it is not clear when the latter word acquired a strict technical meaning, since etymologically (from *viscum*, the mistletoe) it would seem to have been applied originally to liquids possessing the property to an abnormal degree The corresponding terms in French are "frottement intérieur" and "viscosité," and in German "innere Reibung," "Viskosität," and, especially in recent literature, "Zähigkeit," which appears to have been used for the first time by Wiedemann[1] in the strict technical sense.

Newton was the first to formulate a hypothesis regarding the magnitude of the force required to overcome viscous resistance and to treat a case of motion in a viscous fluid. Newton's hypothesis is given in most text-books of physics,

but the peculiar problem chosen and the unfamiliar method
of treatment appear sufficiently interesting to justify quota-
tion *in extenso* of the chapter in question (*Principia*, Lib. ii,
Sect. ix).

"*On the Circular Motion of Liquids*

HYPOTHESIS

*That the resistance which arises from the lack of slipperiness
of the parts of the liquid, other things being equal, is proportional
to the velocity with which the parts of the liquid are separated
from one another.*

Proposition LI.   Theorem XXXIX

*If a solid infinitely long cylinder in a uniform infinite liquid
revolve round its axis with uniform motion, and the liquid be
caused to revolve by the impulse thereof only, but every part of
the liquid persevere uniformly in its motion; I say that the
periodic times of parts of the liquid are as their distances from
the axis of the cylinder.*

Let AFL (fig. 1) be a cylinder revolving uniformly round
the axis S, and let the liquid be divided by concentric circles
BGM, CHN, DIO, EKP, etc., into innumerable concentric
solid cylindrical shells of the same thickness. And as the
liquid is homogeneous, the impressions made by contiguous
shells on each other will (*ex hypothesi*) be as their mutual
translations and as the contiguous surfaces in which the
impressions are made. If the impression on any one shell
is greater or smaller from the concave part than from the
convex one, the stronger impression will prevail, and will
accelerate or retard the motion of the shell, according as it
is directed in the same or in the opposite sense as its own
motion. If, therefore, any one shell is to persevere uniformly
in its motion, the impressions from either part must be equal
and opposite to one another.* Hence, since the impressions
are as the contiguous surfaces and their relative translations,

---

* For the error in this assumption, and consequently in the result, see
Stokes, p. 10.

the translations will be inversely as the surfaces, *i.e.* inversely as the distances of the surfaces from the axis. But the differences of the angular motions round the axis are as these translations divided by the distances, or directly as the translations and inversely as the distances; that is, combining the ratios, inversely as the squares of the distances. Therefore, if at the several points of the infinite straight line SABCDEQ perpendiculars A*a*, B*b*, C*c*, D*d*, E*e*, etc., be erected and made
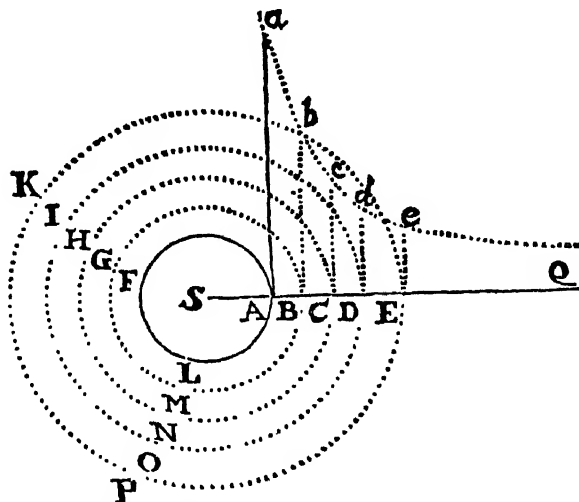
Fig. 1.—Newton's diagram illustrating $\int dr/r^2$. (From *Principia*, 2nd ed., 1713)

inversely proportional to the squares of SA, SB, . . ., etc., and if a hyperbolic curve be imagined drawn through the ends of the perpendiculars, the sums of the differences, *i.e.* the total angular motions, will be as the corresponding sums of the lines A*a*, B*b*, etc., that is, if, to constitute a uniformly liquid medium, the number of circles is increased, and their width reduced, to infinity, as the hyperbolic areas A*a*Q, B*b*Q, C*c*Q, etc. And the times inversely proportional to these angular motions will also be inversely proportional to these areas. The periodic time of any one part D is therefore inversely as the area D*d*Q, *i.e.* (from known quadratures of curves) directly as the distance SD.   Q.E.D.

Corol. 1.   Hence the angular motions of parts of the liquid

are inversely as their distances from the axis of the cylinder and the absolute velocities are equal.

Corol. 2.   If a liquid be contained in an infinitely long cylindrical vessel and contain another interior cylinder; if both cylinders revolve about their common axis and the times of their revolutions be as their radii, and if every part of the liquid persevere in its motion, the periodic times of every part of the liquid will be as its distance from the axis of the cylinder.

Corol. 3.   If any common angular motion be added to, or withdrawn from, the cylinder and liquid moved in this manner, the motion of the parts against one another will not change, as the mutual friction of the parts of the liquid is not changed. For the translation of the particles against one another depends on the friction. Every part will persevere in that motion which is not more accelerated than retarded by the friction acting from either side in opposite directions.

Corol. 4.   Therefore, if the whole system of cylinders and liquid be deprived of all angular motion of the outer cylinder, there will be motion of the liquid in the cylinder at rest.

Corol. 5.   Hence, if the interior cylinder be rotated uniformly, the liquid and the outer cylinder being at rest, the rotary movement will be communicated to the liquid and will gradually be propagated through the whole of it, nor will it cease to increase until the several parts of the liquid acquire the motion defined in the fourth corollary.

Corol. 6.   And because the liquid tends to propagate its motion yet further, the outer cylinder will also be carried round by it unless forcibly detained, and its motion will be accelerated until the periodic times of both cylinders become equal. If the outer cylinder be forcibly detained, it will tend to retard the motion of the liquid, and, unless the inner cylinder by some force impressed from outside maintain it, will gradually cause it to cease.

All which may be tried in deep and stagnant water.''

Newton's fundamental assumption amounts to the following : If two laminæ having an area of contact A move with constant velocities v_1 and v_2, the force required to maintain

the constant difference of velocity is

$$F = \eta A \frac{(v_1 - v_2)}{(z_1 - z_2)},$$

in which the z are measured in the direction perpendicular to the laminæ. Since the velocity in the liquid changes continuously, we may replace the differences by differentials and write:

$$F = \eta A \frac{dv}{dz} \quad . \quad . \quad . \quad . \quad (1)$$

in which, as experience has shown, η is a characteristic constant for each liquid, which, at ordinary pressure, decreases with temperature, but in all simple liquids and true solutions is independent of dv/dz.

By introducing the dimensions in equation (1),

$$[F] = [MLT^{-2}] \quad [A] = [L^2] \quad [dv] = [LT^{-1}] \quad [dz] = [L],$$

we find the dimensions of η to be

$$[\eta] = [ML^{-1}T^{-1}].$$

η is called the coefficient of viscosity, and its physical meaning becomes clear if the factors on the right hand of equation (1) are chosen $=1$. The viscosity coefficient is the force required per unit area to maintain unit gradient of velocity, or the force required per unit area to maintain unit difference of velocity between two parallel planes in the liquid unit distance apart. The coefficient is usually expressed in dynes, centimetres and seconds, and the value $\eta = 1\cdot000$ in these units is conveniently called a Poise (in honour of Poiseuille (see below)), and its hundredth part a Centipoise; the coefficient of viscosity of water at 20° is approximately a centipoise.

The reciprocal of the viscosity is called the fluidity, ϕ, and is generally expressed as $1/(\eta$ in poises).

The dimensions of the velocity gradient (which assumes considerable importance in anomalous liquids, such as the majority of colloidal solutions) are $[T^{-1}]$. The only unambiguous way of expressing it is to state the change in

velocity per unit distance measured at right angles to the direction of the velocity: $\pm n$ cm. per sec./cm. Several authors [2] express the velocity gradient in "radians per second," one radian per second being taken as unit gradient. This is perhaps a convenient method of avoiding the somewhat cumbersome expression given above, and unobjectionable as far as dimensions are concerned, but hardly conveys the idea of a gradient.

Although Newton's hypothesis thus leads to an equation which, as will be shown later on, can be applied directly to important cases of motion in viscous liquids, the hydrodynamics of the following century, as developed by Daniel Bernoulli, Euler and others, was exclusively concerned with ideal liquids, in which tangential forces between adjacent parts of the liquid were excluded. Even simple experiments could not fail to reveal very considerable discrepancies between the results of theory and the behaviour of real liquids, speaking of which Bernoulli [3] says in his *Hydrodynamica*: " I attribute these enormous differences for the greatest part to the adhesion of the water to the sides of the tube, which adhesion can certainly exert an incredible effect in cases of this kind."

The numerous and extensive investigations on the flow of liquids in pipes and open channels, carried out by the French engineers and physicists at the end of the eighteenth and the beginning of the nineteenth century, had produced a great mass of material which the hydrodynamics of ideal liquids failed to explain. Prony,[4] who studied the subject both theoretically and experimentally, comments on the lack of interest exhibited by the mathematical physicist : " It is regrettable, and even astonishing, that the celebrated Euler, who in the course of his immense labours has often turned his attention to physico-mathematical problems and their practical applications, should not have endeavoured to treat the theory of liquids by taking into account the cohesion of the molecules and some kind of friction; even if he had introduced these resistances into the analysis in a purely hypothetical form, it would be interesting to know how he envisaged their effect; but I do not know of any paper by him where they are mentioned."

The investigations mentioned above had led to the general result, that the resistance to the flow of liquids in cylindrical tubes could be expressed as the sum of two terms, one containing the first power and the other the square of the velocity.

The problem whether this second term becomes negligible when the motion is very slow, was attacked by Coulomb [5] in an entirely new way. Although he quotes Newton (*Princ.*, Lib. ii, Prop. 40) on the slow fall of spheres in air or water, he makes no reference to the hypothesis in Prop. 51. Coulomb's method consisted in causing a horizontal circular disc suspended from a wire to oscillate round its axis in air and in the liquid to be examined; the resistance of the latter was deduced from the logarithmic decrement of the amplitude. The resistance for slow motion was found to be simply proportional to the velocity, and, other things being equal, to the fourth power of the radius. Coulomb deduces from his experiments a "resistance factor," viz. the force required per unit area to maintain unit velocity (which has a meaning for the particular apparatus used only).

Coulomb found that the same relations as for water held for "a clarified lamp oil," the resistance factor of which turned out to be 17·5 times that of water. He made two further series of experiments, which, as he says, might have a bearing on future theories of the nature of liquids.

The first series was undertaken for the purpose of ascertaining whether the nature of the surface in contact with the liquid affected the results. The disc was first covered with a thin layer of tallow, which did not cause any change in the logarithmic decrement; the greased disc was then covered with a thin coat of powdered stoneware, and the decrement still remained unaltered.

The second series was directed to ascertaining whether pressure altered the frictional resistance. Coulomb points out that any difference in pressure due to varying the depth of liquid above the disc would be negligible compared with atmospheric pressure, and therefore carried out a number of determinations in a vacuum. No difference could be detected, whence Coulomb concludes that the frictional resistance is

independent of pressure, and emphasises the difference between
friction in liquids and that between solids.

Coulomb quite clearly points out the advantages of his
method, which allows small forces or moments to be measured
with accuracy. Nevertheless Girard,[6] although he quotes
Coulomb's paper, once more returned to the problem in its
familiar form, and again attempted to determine the law
of flow through cylindrical tubes. By *a priori* reasoning he
arrived at the conclusion that with very slow flow in small
tubes the resistance should be simply proportional to the
velocity, and proceeded to test it with copper capillaries (drawn
over steel wire) of 0·183 and 0·296 cm. diameter; they were
made in 20 cm. lengths, and could be joined by screw couplings
to make lengths up to 2200 cm. His results were best re-
presented by the equation

$$Q = C\frac{d^3 p}{l}$$

(Q =volume discharged in unit time, C a constant, *d* diameter
and *l* =length of tube, *p* =pressure).

Girard also followed Dubuat [7] in studying the influence of
temperature on flow; he found that the resistance decreased
with rising temperature, and that the rate of decrease was
greater at low temperature.

Girard seeks the cause of the resistance purely in the con-
ditions at the wall of the tube, and not in the body of the
liquid. He assumes that a film of liquid adheres firmly to
the wall of the tube, and gives rise to two kinds of resistance:
one is " the force with which all the molecules of the peri-
meter adhere to the liquid layer which envelops and wets the
wall." This resistance is simply proportional to the velocity,
and would be the only one if the wall were absolutely smooth;
its asperities, however, are reproduced in the liquid film and
give rise to turbulence, which produces a second resistance
term containing the square of the velocity. This insistence
on the surface condition of the wall is striking, in view of
Coulomb's negative results.

Up to this time (1813) there had been no attempt to find
a general solution of the problem of motion in viscous liquids

corresponding to the general hydrodynamic equations for ideal liquids developed during the eighteenth century. Such equations were deduced for the first time by Navier [8] ten years later. It is not possible to say more of them here than that they contain, in addition to the density, which alone appears in the equations of the ideal liquid, a second characteristic constant, which is very clearly defined by Navier:

" Let us assume that the velocities of the molecules of liquid contained in the same layer parallel to the plane " (on which the liquid is assumed to rest) " are equal among themselves, and further that the velocities of all layers, as they are more and more distant from the plane, increase progressively and uniformly in such a way that two layers whose distance from each other is equal to the unit of length have velocities whose difference is also equal to the unit of length. On this assumption the constant ϵ (=our η) represents in units of weight the resistance arising from the slipping over each other of any two layers, for an area equal to the unit of surface."

The definition is exactly that of the coefficient of viscosity as it is deduced from Newton's hypothesis.

Navier attempted to integrate the equations for the flow through a cylindrical tube, but obtained the incorrect solution that the volume discharged in unit time, other things being equal, was proportional to the cube of the radius—a solution which appeared to be confirmed by Girard's results.

The equations found by Navier were again deduced by Poisson [9] from different assumptions, and finally by Stokes [10] by a method differing from those of both his predecessors. Stokes integrated them for two cases of great importance: stationary flow through a cylindrical tube, and stationary motion between two coaxial cylinders. The cylinder revolving in an infinite liquid is a special case of the second problem, and Stokes remarks in reference to it: " These cases of motion were considered by Newton (*Princ.*, ii, 51). The hypothesis which I have made agrees in this case with his, but he arrives at the result that the velocity is constant, not that it varies inversely as the distance. This arises from his having taken, as the condition of there being no acceleration or retardation

of an annulus, that the force tending to turn it in one direction must be equal to that tending to turn it in the opposite direction, whereas the true condition is that the moment of the force tending to turn it in one direction must be equal to the moment of the force tending to turn it in the opposite direction.   Of course, making this alteration, it is easy to arrive at the above result by Newton's reasoning."

While the mathematical theory had taken its final shape, experimental investigation had likewise made important progress.   In 1839 Hagen [11] studied the flow of water at different temperatures through brass tubes of the following dimensions:—

Length (cm.).	Radius (cm.).
47·20	0·127
108·70	0·207
104·40	0·294

The pressure was produced by a head of water, and the quantity discharged was determined by weighing. Hagen found that the volume discharged in unit time was proportional to the pressure, to a power of the radius and inversely proportional to the length of the tube. The exponent, calculated by the method of least squares, was found to be 4·12, and Hagen suggested that the true value was 4. He also made observations on the departures from this law, which he ascribed to turbulence, and noticed that, other things being equal, turbulence set in more easily at lower viscosities, *i.e.* at higher temperatures.

Hagen's work, although practically a complete anticipation, has been overshadowed by that of Poiseuille,[12] a short abstract of which appeared in the *Comptes Rendus* of 1842, his first paper being printed *in extenso* in 1846.   No doubt this is largely due to the extraordinary completeness and elegance of the investigation, which still deserves careful study, and the fortunate accident that Poiseuille approached the problem as a physician interested in the circulation of blood in capillary vessels, and not as a hydraulic engineer; he accordingly used (glass) capillaries of very much smaller bore than any of his predecessors, and had to deal with

purely laminar flow. He used five capillaries with the following diameters:—

A, 0·14 mm.;   B, 0·113 mm.;   C, 0·085 mm.;
D, 0·044 mm.;   E, 0·03 mm.

Long series of measurements were carried out, in each of which one of the relevant factors only was varied at a time. The capillaries were joined to a bulb, and a constant volume defined by marks above and below the bulb forced through them by compressed air. The results were:

1. The quantity discharged in unit time is proportional to the pressure, provided the length of the tube exceeds a certain minimum, which increases with the radius.

2. The quantity discharged in unit time is inversely proportional to the length of the tube.

3. The quantity discharged in unit time is directly proportional to the fourth power of the radius.

The quantity discharged in unit time is therefore

$$Q = K\frac{PD^4}{L},$$

where K is a constant characteristic of the liquid, the value of which increases with temperature. Poiseuille carefully investigated the variation of K, and gave a formula containing two constants for calculating its value at any temperature.

The meaning of the constant K became clear when Wiedemann [13] and Hagenbach,[14] independently of each other, deduced mathematically the expression for the volume passed in unit time. Both make use of Newton's hypothesis without referring to him, or to Stokes's deduction of the velocity of flow. They obtained the equation

$$Q = \frac{\pi PR^4}{8\eta L},$$

in which η is a constant characteristic of the liquid, which Wiedemann proposed to call the " Zähigkeits-Koeffizient," *i.e.* the coefficient of viscosity. Hagenbach defines it as follows: " We designate by the name Viscosity (Zähigkeit)

the force necessary for shifting a layer of liquid of unit area and of the thickness of one molecule past a second layer by the distance of two molecules in unit time." The definition does not appear very useful as it stands, but as the thickness of a layer and the distance of two molecules in it are assumed equal, it amounts to postulating unit gradient, and therefore agrees with the accepted definition. Hagenbach calculated η from Poiseuille's data, and, taking the gramme and square metre as units, found for water at 10°,

$$\eta = 0 \cdot 13351.$$

Hagenbach mentions the interesting fact that practice had been in advance of theory, inasmuch as it had been found desirable in the arts to characterise certain liquids empirically by their viscosity. Dollfus [15] is stated to have used an instrument called a " viscosimeter " for testing the gum solutions used in cotton printing, while Schübler,[16] in a paper on " The Fatty Oils of Germany," included among their physical constants the " fluidity ratio " (Flüssigkeits-Verhältnis). The instrument used by him was not much inferior to some still in use for technical purposes: it consisted of a glass cylinder about 10 cm. long and 1·8 cm. diameter, with a tapering outlet of about 1·8 mm. diameter. A constant volume of liquid was charged into the instrument, and the time in seconds it took to empty read by a watch. The " fluidity ratio " is the inverse ratio of the times of efflux, water being taken as standard liquid and its " fluidity " as 1000. Determinations were made at two temperatures—7·5" and 15" C. The " fluidity " of, e.g., castor oil was found to be 2·6 at 7·5" C. and 4·9 at 15° C.

The work of Wiedemann and Hagenbach gave the interpretation of Poiseuille's results, and made it possible to determine viscosity in absolute measure, but theory was still incomplete in one particular. There is nothing in the deduction to indicate that the assumptions on which it rests cease to hold good at some limiting values of pressure or dimensions; both Hagen and Poiseuille, however, had found experimentally that the linear relation between discharge and pressure no longer held when the pressure was raised beyond, or the length

of the tube reduced below, a certain limit. This question was settled by the work of Osborne Reynolds,[17] who showed that, with a given tube and liquid, there existed a critical velocity at which the flow changed abruptly from the laminar type, in which each particle moves with constant velocity parallel to the axis of the tube, to the turbulent type, in which the particles move in irregular paths. (Hagen had already clearly expressed the view that some such change in the nature of the flow occurred.) Other things being equal, the critical velocity is proportional, not to the viscosity, but to the viscosity divided by the density, a constant which has since received the name " Kinematic Viscosity."

During the thirty years following Hagenbach's work a considerable number of viscosity measurements by means of various capillary instruments were carried out; several other methods were also developed, the mathematical theory of which is complicated and leads to approximate solutions only. In 1890 Couette [18] took up the system of concentric cylinders, the velocity distribution for which had already been given by Stokes, who suggested that it might be studied experimentally by observing " motes in the liquid." Couette calculated the moment exerted by the outer cylinder on the inner one, and constructed an apparatus in which this moment could be measured and the coefficient of viscosity deduced from it; it was found to agree with Poiseuille's values. Couette also found that beyond a certain velocity the linear relation between angular velocity and moment ceased to hold abruptly, and compared this change to that from laminar to turbulent flow in the capillary. He also examined whether a criterion analogous to that given by Reynolds for the tube could be postulated for the concentric cylinder system; while he did not formulate it completely, he showed that, for the somewhat extreme case of water and air, the velocities at which turbulence set in were very approximately proportional to the kinematic viscosities.

The capillary viscometer, however, has remained the most extensively used instrument, and, especially since Ostwald gave it the simple form called after him, has been employed in a very large number of investigations of varying accuracy.

Many of these were undertaken with the object, or in the hope, of finding relations between a physical property so easily measured as viscosity and the chemical constitution of pure liquids; an even greater number have attempted to connect quantitatively the viscosity of electrolyte solutions with their conductivity, or that of mixtures with the viscosities and ratios of the components. All these investigations, more particularly those on liquid mixtures, have had to face the initial difficulty that there is so far no theory of the viscosity of simple liquids. It is not the purpose of this work to discuss such attempts at a theory as have been published beyond saying that, with one exception, they are all of earlier date than the very important work of Bridgman on the variation of viscosity with pressure, and are quite irreconcilable with his results, to explain which will be the first object of any fresh attempt.

The study of viscosity has received a new impetus from the development of colloid chemistry. Here, too, the tendency has been to find relations between the changes in viscosity and changes in other properties less easy to measure or, sometimes, even to define. In this discipline an entirely new, and fundamental, difficulty has arisen, inasmuch as many of these colloidal systems exhibit the striking anomaly that the viscosity coefficient is not a constant, as defined on p. 5, but varies with the velocity gradient. This feature will be fully described in the chapter dealing with colloidal solutions.

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CHAPTER II

MATHEMATICAL THEORY OF THE PRINCIPAL METHODS OF DETERMINING THE COEFFICIENT OF VISCOSITY

THE most widely used method for determining viscosity coefficients is still in principle that of Poiseuille, though many modifications in experimental details have been made by successive observers. The liquid is forced through a capillary tube, and η is deduced from the volume discharged in unit time, the pressure, and the dimensions of the apparatus. The advantages of the method are: the comparative simplicity and cheapness of the apparatus, the small quantity of liquid required for examination, the ease with which it can be maintained at constant temperature, and finally the circumstance that the mathematical theory can be developed with perfect strictness and without approximations.

Flow in a Capillary Tube. As related in the previous chapter, the laws governing the flow of a liquid through a tube of small diameter have been deduced from the hydrodynamic equations by several physicists; the elementary treatment of the problem to be adopted here appears to have been first given by Hagenbach (*loc. cit.*, p. 11). We consider a portion AB of a cylindrical tube having a circular cross-section of radius R (fig. 2). The distance AB = L, and

FIG 2.—Velocity and velocity gradient in capillary tube

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a difference of pressure $=P$ is maintained between A and B, which causes the liquid to flow through the tube. We assume the flow to be such that every particle of liquid moves parallel to the axis of the cylinder with a constant velocity v. For reasons of symmetry this velocity will be the same for all points lying on the same circle, so that we may consider the liquid composed of cylindrical laminæ moving with velocities which are functions of their radii.

The force exerted by the pressure P on a cylinder of radius r is

$$F_P = \pi r^2 P,$$

while the resistance round the surface of the cylinder, caused by the viscosity of the liquid, will, according to our fundamental assumption, be given by the product: area × viscosity coefficient × velocity gradient, *i.e.*

$$F_V = 2\pi r L \eta \frac{dv}{dr}.$$

If the motion of the cylinder is not to be accelerated, *i.e.* if v is to remain constant, the forces acting on the cylinder must be equal and opposite, $F_P = -F_V$, and therefore

$$rP = -2L\eta\frac{dv}{dr} \qquad . \qquad . \qquad . \qquad (1)$$

The velocity gradient is therefore

$$\frac{dv}{dr} = -\frac{rP}{2L\eta} \qquad . \qquad . \qquad . \qquad (2)$$

By integration we find:

$$v = -\frac{r^2 P}{4L\eta} + C \qquad . \qquad . \qquad . \qquad (3)$$

It now remains to determine the integration constant C, for which purpose it is necessary to make some assumption about the conditions at the boundary. The usual assumption is that the lamina in contact with the wall of the tube adheres to it; in other words, that

$$v = 0 \quad \text{for} \quad r = R.$$

The integration constant then becomes

$$C = \frac{R^2P}{4L\eta},$$

and the velocity

$$v = \frac{P}{4L\eta}(R^2 - r^2) \qquad . \qquad . \qquad . \qquad (4)$$

This is the equation of a parabola (fig. 2), the axis of which is the axis of v, while the axis of r is at the distance $R^2P/4L\eta$ from the apex of the curve. Since v is the distance travelled in unit time, the particles of liquid which were in the plane AA at zero time will be on the surface of the paraboloid, the profile of which is given by equation (4) after unit time; in other words, the volume of this paraboloid is the volume of liquid Q which passes in unit time. The volume of this solid of revolution is

$$Q = 2\pi \int_0^R vr\,dr,$$

and by introducing the value of v,

$$Q = \frac{2\pi P}{4L\eta} \int_0^R (R^2 - r^2)r\,dr = \frac{\pi PR^4}{8L\eta} \qquad . \qquad . \qquad (5)$$

This expression is identical with that found empirically by Poiseuille (p. 11); the constant K in his formula accordingly has the value (provided P is expressed in the same units)

$$K = \pi/128\eta, \quad \text{whence} \quad \eta = \pi/128K,$$

by means of which expression the values of η can be calculated from Poiseuille's results, a calculation carried out apparently for the first time by Hagenbach (*loc. cit.*, p. 12).

As the flow is stationary, it follows that the volume Q_t discharged in the time T is

$$Q_t = \frac{\pi PR^4}{8L\eta}T.$$

All capillary viscometers are so designed that a constant volume is passed through the capillary and the time T of dis-

charge is measured. Q_t, R, and L are therefore constants of the instrument, while η at a given temperature is a constant for any normal liquid.   It therefore follows that, if the instrument has such dimensions that Poiseuille's Law holds good, the product PT must be constant, and this relation can be used to test whether the instrument is, in fact, correctly proportioned.   Conversely, once the instrument has been found correct, variation in the value of PT proves that the liquid does not behave normally (see Colloidal Solutions).

Turbulent Flow.   In the deduction of Poiseuille's Law laminar flow has been assumed, but it is impossible to say *a priori* that laminar flow will be maintained whatever the pressure, and therefore the mean velocity $(v = Q/\pi R^2)$, may be. Poiseuille already found, with all his tubes, deviations from the law when the pressure, other things being equal, was increased beyond a certain limiting value.   Osborne Reynolds [1] showed in an exhaustive experimental and mathematical investigation that this deviation—which manifests itself as an apparent increase of η—was due to a change from laminar to turbulent flow; with the latter the particles of liquid no longer move in straight lines, but in irregular paths which change with time.   Reynolds found that, the more viscous the liquid, the less its tendency to form eddies.   The constant which determines the type of flow is, however, not the viscosity coefficient, but the viscosity coefficient divided by the density, η/ρ—an important constant which has since received the name *kinematic viscosity*.[2]   In a given tube the liquid with the lower kinematic viscosity becomes turbulent at lower velocity than that with the higher.

Reynolds further showed that the conditions of flow for any tube and liquid could be characterised by a non-dimensional quantity, *i.e.* a pure number.   The variables affecting the flow in a cylindrical tube can be combined to give such a non-dimensional expression as follows:—

$$R = \frac{vD\rho}{\eta},$$

in which v is the mean velocity and D the diameter of the tube.   R is called the *Reynolds number*; conditions in different

tubes with different liquids will be the same when the Reynolds numbers are the same. More particularly there will be a change from laminar to turbulent flow when R reaches a certain value, which experiment has shown to be 1400 to 2000 for capillaries. The critical velocity is therefore

$$v_c = \frac{2000\eta}{D\rho}.$$

This value of R is the Reynolds criterion for capillaries; the onset of turbulence is hastened by disturbances in the liquid *before* it enters the tube, so that the exact value of the criterion depends on the conformation of the orifice of the tube. By keeping the velocity well below the value corresponding to $R = 1400$, it is generally possible to avoid turbulence.

Even when the flow is laminar inside the tube at some distance from the ends, there are disturbances at the junction between it and the reservoir from which the liquid enters the tube, the exact nature of which need not be discussed. The effect they produce is that the formula—as Poiseuille found experimentally—does not hold strictly except for tubes of such length that the portions in which the flow is not laminar become negligible. A correction can be applied to the formula for these effects, which will be given below.

Kinetic Energy Correction. It has further been assumed that the pressure is balanced by the frictional resistance, but this assumption does not quite correspond with conditions in the usual instruments, as was shown first by Hagenbach and again, in a very detailed study, by Couette.[3] They point out that the formula (5) is strictly correct if a portion of a longer tube is considered, in which the liquid has reached a constant velocity; if, however, as is always done in viscosity measurements, L is taken as the whole length of the tube between two large reservoirs, and P as the difference of pressure between them, a portion only of this pressure serves to overcome viscous resistance, while the balance is used to impart velocity, *i.e.* kinetic energy, to the liquid. This portion can be calculated, and leads to a correction for the value

of η calculated from equation (5), which is

$$\eta = \frac{\pi PR^4}{8LQ},$$

while the value corrected for kinetic energy is

$$\eta = \frac{\pi PR^4}{8LQ} - \frac{mQ\rho}{8\pi L} \qquad . \qquad . \qquad . \qquad . \qquad (6)$$

where ρ is the density of the liquid and m a numerical factor. Hagenbach found the value of m to be $1/\sqrt[3]{2} = 0.793$; Couette, whose calculation has been confirmed by Finkener and Wilberforce,[4] finds $m = 1.00$; and a value of $m = 1.12$ proposed by Boussinesq[5] has been used in a number of investigations.

Couette suggested a second correction to allow for the non-laminar flow at the ends of the capillary, which has been referred to above. This takes the form of a " fictitious lengthening " of the capillary, whereby equation (6) becomes

$$\eta = \frac{\pi PR^4}{8Q(L+\lambda)} - \frac{mQ\rho}{8\pi(L+\lambda)} \qquad . \qquad . \qquad . \qquad (7)$$

The value of λ cannot be deduced theoretically, but must be found by experiment, and is generally of the order of a few diameters. The method by which Couette tested both corrections is generally applicable when L can be varied, and may therefore be described briefly. The results to be corrected were a set obtained by Poiseuille with two short tubes, A and B, of the same bore but different lengths. The values of η at 10° calculated from these by the uncorrected formula vary with the pressure. When the corrected formula (6) is applied the values of η become constant, i.e. no longer vary with the pressure, but the value found with A is different from that found with B, and both differ from the true value found with long tubes. If these differences are due to end effect, and if they can be corrected by adding an amount λ to the length, λ must have the same value for both tubes, since they have the same diameter and the shapes of the ends are the same. The equation

$$\eta_A \frac{L_A}{L_A + \lambda} = \eta_B \frac{L_B}{L_B + \lambda}$$

therefore holds, so that λ can be calculated from a pair of observations:

$$\lambda = \frac{L_A L_B (\eta_A - \eta_B)}{\eta_B L_B - \eta_A L_A}.$$

Considerable divergence of opinion prevails regarding the conditions in which the Hagenbach-Couette correction is applicable. Grüneisen,[6] in a very exhaustive investigation on the range of validity of the Poiseuille formula, finds that it is not justified with instruments in which the capillary ends in large reservoirs, in which the liquid has a free surface of considerable area, since in such arrangements the gain or loss in velocity, and therefore in kinetic energy, is negligibly small. He tests the correction by applying it to a series of results obtained by Poiseuille with one of his longer tubes (R = 0·00567, L = 2·357 cm.), in which the extreme values of the product PT do not differ from the mean value by more than 0·1 per cent. The kinetic energy correction should apply to this tube just as well as to the shorter tubes treated by Couette, since the conditions at the ends were exactly alike in both cases (see fig. 3). Grüneisen, however, shows that its application results in greatly increasing the discrepancies, so that the maximum deviation from the mean value becomes 1·8 per cent.; he considers the agreement obtained by Couette rather accidental.

Graetz, in the chapter Friction in Liquids and Gases of Winkelmann's *Handbuch der Physik*, also expresses the view that the kinetic energy correction is not justified, at least in full, in the instrument used by Thorpe and Rodger (see fig. 9). These authors applied it to all their measurements, but found the λ correction unnecessary. In accordance with Graetz's view, Thorpe and Rodger's results are recalculated and given without the kinetic energy correction in Landolt and Börnstein's Tables, 4th edition; but in the 5th edition the present editor, Erk, adds a footnote (Ergänzungsband, p. 76), stating that later investigation, including work of his own, has shown the correction to be applicable, which should therefore be added to the figures in the tables.

Bingham [7] is emphatic in support of the correction, and

shows that it leads to concordant results. There is no difficulty in calculating the correction (6) when the tube, as in Bingham's improved Thorpe and Rodger instrument, has square ends, so that L is accurately known, while the λ correction can be determined experimentally from two or more lengths of the same tube fixed in the same way into the same reservoirs. The matter, however, becomes more complicated in instruments in which the reservoirs are blown in one piece with the capillary, and the bore, as is recommended by most authors, expands gradually, so that L is indefinite. In such instruments it will generally be simplest to check the constancy of PT, and the way in which the correction can be found is indicated in a general review of the problem by Dorsey,[8] based on data obtained by Bond.[9] Dorsey transforms the equation (7) into

$$PT = \frac{8\eta Q'}{\pi r^4}\left(L + \lambda + \frac{m\rho r^2 v'}{8\eta}\right),$$

where Q' is the volume discharged in time T, and v' the average velocity ($v' = Q'/T\pi r^2$). The third term in brackets also has the dimensions of a length, so that the expression can be written:

$$PT = \frac{8\eta Q'}{\pi r^4}(L + \lambda + \lambda_1),$$

and the problem of finding the correction resolves itself into determining the sum in brackets, so that PT is constant for a given liquid, *i.e.* for a given kinematic viscosity.

The value of $\lambda + \lambda_1$ can be shown from Bond's investigation to depend on the average velocity v'. Bond determined the pressure required to drive equal volumes through two tubes of the same bore, but different lengths L_1 and L_2, discharging always into the same reservoirs, so that the end conditions were the same. The excess pressure P_e necessary to overcome the end effect is therefore the same for both lengths, and we can write:

$$P_1 = L_1 dp/dl + P_e, \qquad P_2 = L_2 dp/dl + P_e,$$

whence

$$P = (L_1 P_2 - L_2 P_1)/(L_1 - L_2),$$

so that P_e, or the additional length corresponding to it, can be deduced from a pair of determinations.

Dorsey concludes from Bond's data for a range of velocities, that for Reynolds numbers $(=2\rho v r/\eta)<10$, $\lambda+\lambda_1$ is independent of v, and $=1\cdot146r$. For Reynolds numbers between 10 and 700 (300 to 800 is a common range) the sum increases in linear ratio with v, and $d(\lambda+\lambda_1)/dv$ is $=0\cdot98\rho r^2/8\eta$, with an error of about 2 per cent. These figures give an idea of the value of the correction, but when L is not exactly known, it must be determined as indicated above.

Effective Head of Liquid. The pressure has been assumed to remain constant during the whole period of flow, and it

FIG. 3.—Poiseuille's viscometer.

remains to be seen how far this constancy is realised in the experimental arrangements usually employed. The pressure is produced either by a column of liquid in the instrument only, or by compressed air. The pressure of the latter can easily be kept constant by the use of an air receiver large in comparison with the volume of liquid to be displaced, and protected from changes of temperature; but in general a small column of liquid, *the length of which varies during the period of flow*, will have to be added to (or subtracted from) the air pressure. Poiseuille, *e.g.*, used the arrangement shown in fig. 3, the bulb A and the capillary being completely filled with, and submerged in, the liquid under examination; measurements were made by applying air pressure and noting the time which the liquid took to fall from mark B to mark B', while at the same time it rose in the outer vessel from C to C' (much exaggerated in the drawing). In this arrangement, with air pressures of the order of atmospheres, the mean height of the variable column of liquid, $(BC+B'C')/2$, may be taken as having acted uniformly during the whole period of flow, and is subtracted from the air pressure.

If the flow is produced merely by a column of liquid, the

height of which varies perceptibly, the small volume dQ discharged during an element of time dt is

$$dQ = \frac{\pi R^4 h g \rho}{8 \eta L} dt \qquad . \qquad . \qquad . \qquad (8)$$

where h is the (variable) head of liquid at the moment, ρ its density, and g the gravity constant. If, now, the portions of the apparatus out of, and into, which the liquid flows have a simple, *e.g.* cylindrical, shape, h can obviously be represented as a function of Q, and the resulting equation can be easily
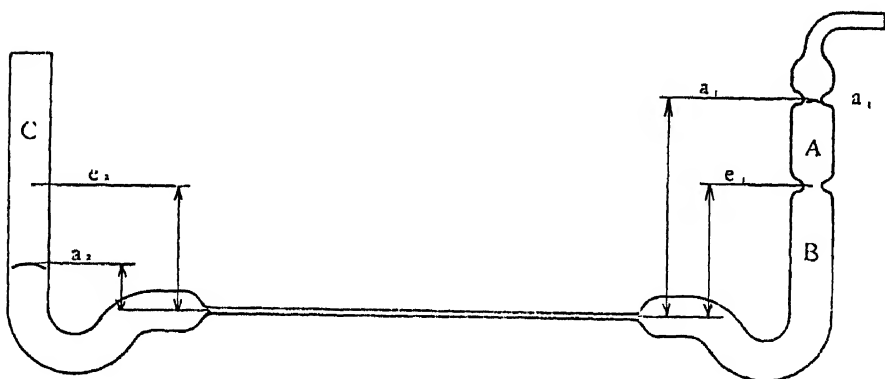
FIG 4.— Koch's viscometer

integrated. This method was adopted by K. R. Koch [10] in a careful determination of the viscosity coefficient of mercury over a considerable range of temperature. His apparatus is shown diagrammatically in fig 4; a_1 and a_2 are the levels at the beginning, and e_1 and e_2 those at the end of the time T, the tubes A, B, and C having the same diameter. The relation between Q and h is

$$Q = \frac{a_1 - a_2 - h}{2} R_1^2 \pi,$$

R_1 being the radius of A, B, and C. By introducing this value in (8) and integrating, we find

$$\eta = \frac{\pi R^4 T[(a_1 - a_2) - (e_1 - e_2)] g \rho}{8 Q L \log_e \dfrac{a_1 - a_2}{e_1 - e_2}} \qquad . \qquad . \qquad (9)$$

The same calculation applies to an instrument designed by Wo. Ostwald and R. Auerbach [11] for the investigation of colloidal solutions. The capillary A (fig. 5) discharges into the wider tube B and the liquid overflows into the funnel C. The level of the liquid is therefore constant at B; a_1 and e_1 are measured from it, while a_2 $e_2 = 0$. The equation for this arrangement thus becomes

$$\eta = \frac{\pi R^4 T (a_1 - e_1) g \rho}{8Q \log_e (a_1/e_1)} \qquad (10)$$

The Ostwald Viscometer. When relative viscosities only are to be determined, the elimination of the variable pressure produced by the decreasing column of liquid becomes possible. The most widely used instrument for this purpose is the (Wilhelm) "Ostwald viscometer," a very usual form of which is shown in fig. 6. A constant volume of liquid is charged into the right-hand limb with a pipette and drawn up into the left limb above the mark A; the liquid is then allowed to flow back,

FIG. 5.—Ostwald and Auerbach's viscometer.

and the time it takes to fall from A to B is taken with a stop-watch generally reading to 0.2 second. The flow may be considered to be caused by an average head h, which is constant, since the volume of liquid used is constant. The average pressure is therefore $hg\rho$, and, combining all the constants into one, we may write: $\eta = C\rho T$. If T, the time between the marks, is determined for one liquid
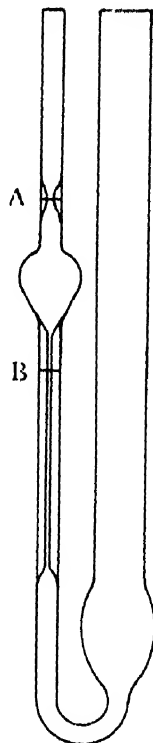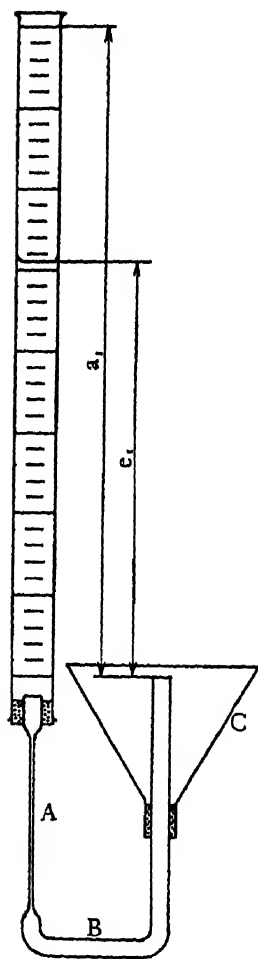
FIG. 6.—Ostwald viscometer (usual form).

of known ρ and η, the viscosity coefficient η' of another liquid of density ρ' can be found by determining the time of fall between the marks, T':

$$\eta' = \eta\frac{\rho'T'}{\rho T} \quad . \qquad . \qquad . \qquad . \quad (11)$$

η' is thus always found as a relative viscosity, whether it be expressed as such by taking $\eta = 1$, or whether the actual value of η be introduced into the equation.

A very large number of investigations has been carried out with instruments substantially of the shape illustrated in fig. 6, and the results have been calculated by the formula (11), which has been assumed to be valid provided the time of efflux of the liquid used in standardising exceeded some arbitrarily chosen limit like 60 seconds. Such a procedure, besides assuming tacitly that the kinetic energy and the λ corrections are unnecessary, neglects some sources of error peculiar to the instrument, which require discussion.

The fundamental assumption on which equation (11) is based is the constancy of the mean head of liquid (whatever function of the initial and final differences of level it may be), which is supposed to be secured by charging a constant volume into the instrument from a pipette. It may be taken for granted that the volume discharged from a properly designed and used pipette is constant [12] to the required degree of accuracy; if the expansion of the glass of both pipette and viscometer can be neglected within the usual temperature range, the volume will still be constant if the pipette is filled with liquid at the temperature of the thermostat in which the measurement is carried out. It has, however, been a fairly common practice, *e g.* in determining temperature-viscosity curves, to fill the viscometer for once and all, and to raise the temperature of the thermostat by suitable steps. In this case the head no longer remains constant, but increases with rising temperature; the necessity of filling at the temperature of measurement, or, alternatively, of readjusting the volume at each temperature, has been pointed out by several investigators, *e.g.* Bingham.[13]

Even assuming constant volume, the mean head differs for

liquids with different surface tensions. In the instrument shown in fig. 6 the liquid at the beginning of timing stands at the upper mark, which is placed on a constriction in the tube; at the end it stands at the lower mark, which is actually on the capillary. The hydrostatic head at either mark is therefore not simply equal to the difference in level between the marks and the corresponding liquid levels in the right-hand limbs, but to these differences *minus* the capillary rises corresponding to the diameters at the two marks. While the level falls in the bulb itself, which is approximately of the same diameter as the right-hand limb, both being large enough to neglect capillary effects, the effective head is equal to the difference in level, but as the liquid sinks into the lower conical portion of the bulb, the surface-tension effect gradually increases to a maximum, which is reached at the mark. The sum total of this effect is that the mean effective head is equal to the mean difference in level *minus a quantity proportional to the surface tension of the liquid, and therefore different for different liquids.*

The volume and the surface-tension error can be practically eliminated by improved design, which will be discussed in the next chapter. The question whether kinetic energy or length corrections are necessary, or whether a given instrument is so proportioned that Poiseuille's Law holds for a certain range of kinematic viscosity, can be decided by experiment only, which may be carried out in two ways. The first is to determine the relative viscosities of a number of liquids and to compare them with the ratios calculated from accepted values. The second consists in varying the pressure and checking the constancy of the product PT; the variable pressure is generally air pressure, to which is, of course, added the mean pressure of the liquid, *i.e.* the mean head multiplied by the density. The mean head must therefore be known, and is slightly different from the arithmetical mean of the initial and final head. If the bulb were cylindrical and of the same diameter as the right-hand limb, the formula (10) would obviously apply, and the mean head of liquid would be

$$H_m = \frac{a_1 - e_1}{\log_e (a_1/e_1)}.$$

This formula is sometimes given in the literature,[14] but does not apply unless the two limbs are cylindrical and equal, as this relation is assumed in expressing the variable head as a function of Q. Grüneisen (*loc. cit.*) has determined the mean head experimentally in the following way: a number of marks were placed on the bulb between the two marks defining the volume, and the pressures exerted by the column of liquid, when standing at these marks, measured by a manometer. The manometer readings, corrected for temperature, zero, etc., were plotted against the time and the mean ordinate calculated from the area of the diagram. Grüneisen found in this way that the mean pressure was equal, with a negligible error, to the pressure at mean time. Applebey,[15] and Washburn and Williams,[16] who tested Ostwald viscometers specially designed to give high accuracy for the constancy of PT, have confirmed this value of the mean effective head. The experimental method used in applying the test will be described in the next chapter.

The determination of the density of the liquid, which is necessary with the Ostwald instrument, is avoided in viscometers designed by Ubellohde[17] (fig. 7) and by Bingham[18] (fig. 11, p. 41). In these the flow is produced by air pressure; the two bulbs are as nearly as possible of the same capacity and placed on the same level. The viscometer shown in fig. 7 is filled by suction so that the liquid stands at the marks *a b'*, and it is then forced through by air pressure, the time between the marks *b' a'* being taken. If the time and pressure for a standard liquid with the viscosity η are T and P, the viscosity of another liquid is
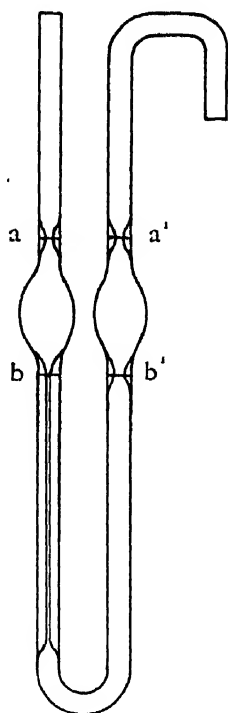
Fig 7 —Ubellohde's viscometer

$$\eta' = \eta \frac{P'T'}{PT}.$$

Bingham himself used this instrument for absolute determination in the manner described in the next chapter.

The Concentric Cylinder System. A second arrangement for which an exact mathematical theory can be developed is that of two vertical coaxial cylinders, between which a liquid is contained; if, *e.g.*, the outer cylinder rotates at constant speed, the liquid assumes a stationary rotary motion and tends to communicate it to the inner cylinder (*cf.* Newton's *Corol.* 5 and 6, p. 4). A certain couple will therefore be required to keep this cylinder at rest, which may be produced by the torsion of a wire from which the inner cylinder is suspended; in this form the arrangement was first used by Couette (*loc. cit.*) for determining viscosity coefficients. The theory had been developed by Stokes from the hydrodynamic equations; the elementary treatment given here appears to be due to Poynting and Thomson.[19]

We consider a vertical length L of the inner cylinder, of radius R_1, suspended coaxially in the outer cylinder, of radius R_2, which rotates with the constant angular velocity Ω. The liquid between the two cylinders will be set in motion,

FIG. 8.

and, when a stationary condition has been reached, each circle of radius r will revolve with constant angular velocity ω. If we consider any such circle, the condition that no acceleration takes place is obviously that the moment maintaining rotation is equal to the moment due to the viscous resistance. This moment is the product area × viscosity coefficient × velocity gradient × radius. The expression for the velocity gradient is found as follows (fig. 8): P and Q are points on two of the concentric circles, in which the liquid moves, lying on the same radius; after a time T the point P has come to P' and Q to Q'; the radius through P' intersects the outer circle at Q''. The velocity gradient at P will then be $=(Q'Q''/T)/P'Q''$; if ω is the angular velocity on the circle containing P, and $\omega + \Delta\omega$ that of Q, then Q'Q'' is $OQ' \Delta\omega T$. Let $OP=r$, $OQ=r+\Delta r$; then $P'Q''=\Delta r$, and the velocity gradient at P is $(r+\Delta r)\dfrac{\Delta\omega}{\Delta r}$, or, when Δr is very small,
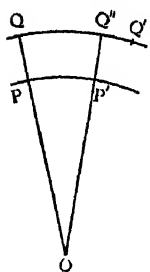
$r\dfrac{d\omega}{dr}$.   The moment due to viscous resistance is thus

$$M = 2\pi r L\eta \,.\, r\dfrac{d\omega}{dr}\,.\,r = 2\pi L\eta r^3 \dfrac{d\omega}{dr}.$$

Since r may be taken anywhere, this expression must be a constant for the apparatus, and equal to the moment maintaining rotation. By integration we find:

$$-\dfrac{M}{r^2} = 4\pi L\eta\omega + C.$$

Since the outer cylinder rotates with the constant angular velocity Ω, while the inner one is prevented from rotating, we have the following conditions at the boundaries:—

for $r = R_2$, $\omega = \Omega$;   for $r = R_1$, $\omega = 0$,

from which the value of the integration constant is found:

$$C = -\dfrac{M}{R_1{}^2}.$$

The moment is accordingly:

$$M = 4\pi L\dfrac{R_1{}^2 R_2{}^2}{R_2{}^2 - R_1{}^2}\eta\Omega = K\eta\Omega \qquad .\qquad . \quad (11)$$

in which K is an apparatus constant.

M is usually measured by suspending the inner cylinder from a wire of known restoring moment N and determining the angle θ by which it is deflected. We then have:

$$N\theta = M = K\eta\Omega\,;$$

or, since N is also a constant for a given wire,

$$\theta = K'\eta\Omega\,;$$

i.e. for a given liquid at constant temperature the deflection is directly proportional to the angular velocity. If the deflections θ and θ' are found for two different liquids at the angular velocities Ω and Ω', the relation between the viscosities is

$$\eta' = \eta\dfrac{\theta'\Omega}{\theta\Omega'}.$$

The linear relation between deflection and angular velocity holds up to a certain limiting value of the latter only, as was first shown by Couette. Beyond this limit turbulence sets in, and the deflection not only increases more rapidly than the angular velocity, but becomes rather irregular. From the experiments of Couette, and later ones by Mallock,[20] a Reynolds number for the coaxial cylinder system can be deduced; the critical angular velocity is

$$\Omega_c = \frac{1900\eta}{(R_2{}^2 - R_1 R_2)\rho},$$

where the factor 1900 again has no dimensions.

It is of interest, in view of some theoretical applications, to determine the velocity gradient in this arrangement. The angular velocity ω on any radius r is found as follows: since the moment is constant for any radius, we can write:

$$M = 4\pi L \eta \frac{R_1{}^2 R_2{}^2}{R_2{}^2 - R_1{}^2}\Omega = 4\pi L \eta \frac{R_1{}^2 r^2}{r^2 - R_1{}^2}\omega;$$

$$\omega = \Omega \frac{1/R_1{}^2 - 1/r^2}{1/R_1{}^2 - 1/R_2{}^2} . \qquad . \qquad . \qquad . \qquad . \quad (12)$$

The velocity gradient finally is

$$r\frac{d\omega}{dr} = 2\Omega \frac{1/r^2}{1/R_1{}^2 - 1/R_2{}^2} \qquad . \qquad . \qquad . \quad (13)$$

In deducing equation (11) we have taken into account a length L of the inner cylinder. In practice, of course, both the outer and the inner cylinders have to be closed at the bottom, so that the moment tending to twist the inner cylinder is not due exclusively to the drag of the liquid between the cylindrical surfaces. If the formula is to apply, the effect of the end faces must be eliminated; the means adopted to achieve this end will be described in the next chapter.

Oscillating Sphere and Disc. A number of other methods for determining η need receive passing mention only, as they have not found extensive application; their mathematical theory is extremely complicated and generally in-

volves simplifications, in consequence of which the results show rather considerable deviations from the most reliable data obtained by the transpiration method. Helmholtz and Piotrowski [21] caused a hollow metal sphere filled with liquid and suspended from a wire to perform torsional oscillations, and determined their period and logarithmic decrement; from these figures and the constants of the apparatus η can be deduced by very complicated calculations. The value found for the viscosity coefficient of water at 24·5° is over 20 per cent. higher than Poiseuille's figure for the same temperature. Meyer [22] used a horizontal circular disc suspended axially by a wire and oscillating in its own place in the liquid; the mathematical treatment is approximate only, as merely the cylinder of liquid, of which the disc is the cross-section, is taken into account, while the motion is propagated into the liquid beyond this boundary. The values of η determined by Meyer, as well as by other investigators [23] using the same method, are higher than those found by the transpiration method; a correction proposed by König [24] reduces the discrepancies to about 1 per cent.

A method used by Mützel,[25] the mathematical theory of which was also developed by Meyer,[26] somewhat resembles that used by Helmholtz and Piotrowski. A hollow cylinder filled with the liquid and suspended by a bifilar suspension is caused to oscillate round its axis and the viscosity coefficient deduced from the logarithmic decrement.

In the investigations just mentioned, the object has been rather to verify experimentally the results of very difficult mathematical deductions than to devise convenient methods for the determination of viscosity coefficients. The solution of an equally or more difficult problem by Stokes [27] has, on the other hand, provided a comparatively simple method of measuring viscosity coefficients, which has found increasing application, especially for very viscous liquids.

Stokes's Formula. Stokes shows that a sphere impelled by a constant force F in a viscous liquid eventually assumes a constant velocity V, and that the following linear relation holds:—

$$F = 6\pi\eta rV \quad . \qquad . \qquad . \qquad . \quad (14)$$

3

where r is the radius of the sphere. The most important special case, as far as the determination of viscosity coefficients is concerned, is that in which the sphere falls (or rises) through the liquid owing to its weight (or buoyancy). The force then becomes

$$F = \frac{4}{3}\pi r^3 g(\rho - \rho'),$$

in which g is the gravity constant ($=980$ cm./sec.^{2}) and ρ and ρ' the densities of the sphere and the liquid respectively, and by introducing this value in (14) we obtain the equation known generally as Stokes's formula:

$$V = \frac{2r^2(\rho - \rho')g}{9\eta} \qquad . \qquad . \qquad . \qquad . \quad (15)$$

This equation enables us to deduce the viscosity coefficient from the observed velocity of fall of a sphere of known mass and radius in a liquid of known density, provided a number of conditions assumed in deducing the formula are satisfied. These are:

(1) The velocity is so small that higher powers of it may be neglected.

(2) There is no slip between the liquid and the surface of the sphere.

(3) The liquid is infinitely extended.

As regards (1), Rayleigh [28] has deduced a criterion by comparing the rates at which the terms included and those neglected in Stokes's deduction tend to decrease; according to him the velocity is small when

$$R = \frac{r\rho V}{\eta} < 1 \qquad . \qquad . \qquad . \qquad . \quad (16)$$

The liquid being given, either r or V may be chosen and the other quantity calculated to satisfy the criterion (16). In practice it will generally be necessary to choose V, so that it can be measured accurately with the particular experimental arrangements to be used, and to adjust the radius to it.

Arnold,[29] in the course of an exhaustive experimental in-

vestigation, has introduced the concept of the "critical radius," which he defines as follows:—

$$\frac{r_c \rho V}{\eta} = 1; \qquad r_c = \frac{\eta}{\rho V}.$$

He finds, as the result of numerous determinations with spheres of different materials and diameters in liquids of widely varying viscosities, that no deviation from Stokes's Law (greater than the experimental error of about 1 per cent.) occurs when

$$r < 0.6 r_c.$$

As regards (2) this condition may be taken to be satisfied, since it is also assumed both in the capillary and the concentric cylinder apparatus, and there is a considerable weight of evidence to show that no slip occurs; experiments by Arnold (*loc. cit.*) and other observers with spheres of different surface finish confirm this evidence.

On the other hand, it is obvious that condition (3) cannot be satisfied experimentally, and some of the earlier attempts to verify Stokes's formula [30] already proved that the walls of the containing vessel exerted a very marked disturbing influence. The only practicable form of boundary or vessel for which the exact mathematical theory has been developed is the cylinder; this was treated by R. Ladenburg.[31] For an infinitely long cylinder and a sphere falling along its axis, the formula becomes:

$$\eta = \frac{2r^2(\rho - \rho')g}{9V(1 + 2 \cdot 4r/R)}$$

The correction term $(1 + 2 \cdot 4r/R)$ does not contain the viscosity coefficient, so that the times of fall with a given tube and sphere (provided, of course, that the radius of the latter conforms to the criterion (16)) are directly proportional to the viscosities, and the arrangement may therefore be used for determining relative viscosities. Since the ratio only of the two radii enters into the correction term, the results obtained with two sets of spheres and tubes having the same ratio are also comparable.

Although in Ladenburg's experiments the distance through which the time of fall was measured amounted to one-half only of the total length of the tube, the ends still exerted a small disturbing effect. To eliminate it, Ladenburg introduced a second term—which, however, applies only to apparatus of approximately the dimensions employed by him—making the complete formula

$$\eta = \frac{2r^2(\rho - \rho')g}{9V(1 + 2\cdot4r/R)(1 + 3\cdot1r/L)}.$$

Ladenburg tested this formula on a liquid of high viscosity (a mixture of 3 parts of rosin and 1 of turpentine), and found that it gave values of η constant within the limits of experimental error. Arnold (*loc. cit.*) found that Ladenburg's formula held equally well for liquids of very much lower viscosities (which were also determined by the capillary method), provided r/R was less than $1/10$.

Glaser [32] investigated the same mixture of rosin and turpentine as used by Ladenburg in a capillary instrument, and his results indicate that at very low velocity gradients this mixture behaves anomalously; the limit below which the anomaly appears was evidently not approached in Ladenburg's experiments.

Stokes's formula applies to undeformable spheres only, which of course are the only ones used for determining viscosities. It is, however, of interest to consider very briefly the behaviour of fluid spheres, such as gas bubbles or liquid globules suspended in a liquid. In these cases flow also takes place within the spheres and modifies the motion; the mathematical treatment has been briefly indicated by Stokes and carried out by Bond.[33] The formula for the velocity becomes:

$$V = \frac{1}{k}\frac{2(\rho' - \rho)gr^2}{9\eta}.$$

k is defined by the equation

$$k = \frac{2/3 + \eta'/\eta}{1 + \eta'/\eta},$$

in which η' is the viscosity of the liquid forming the globules, and η that of the liquid in which they are suspended. When η'/η becomes very large, k approaches 1 (solid spheres); when η'/η becomes small, k approaches 2/3 and $1/k$ approaches 1·5. Bond tested the formula with air bubbles in sodium silicate solutions of different concentrations and in golden syrup; also with globules of syrup in castor oil. The values of $1/k$ thus found are in good agreement with the theoretical figure.

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CHAPTER III

THE DESIGN AND USE OF VISCOMETERS

A. Capillary Viscometers. These fall naturally into two classes: (1) instruments for determining absolute viscosities directly from the dimensions of the instrument and from the experimental data, and (2) instruments for determining relative viscosities by reference to suitable standard liquids.

(1) The apparatus of this class, of which Poiseuille's was the first, has chiefly an historical interest, as so many accurate data are now available that further ones may safely be determined as relative values. The first convenient instrument departing markedly from the arrangement used by Poiseuille was designed by Thorpe and Rodger and employed in an extensive investigation of organic liquids; [1] it is illustrated in fig. 9. The horizontal capillary CD is fused into the thin glass sleeves connecting the bulbs L and R; its dimensions are: R=0·00820 cm., L=4·9326 cm. Each vertical limb has one large and two small bulbs, and in addition a trap (T_1, T_2); marks are placed at m_1, m_2 and K_1 on the left, and at m_3, m_4 and K_2 on the right-hand limb. The liquid is charged into the instrument from a small flask, into which it has previously been distilled, by means of a long thin tube passing through H_2 down into R; the volume is then adjusted by applying air pressure to the left-hand limb, until the liquid stands at K_1, and any excess overflows at H_2 into T_2. The liquid is then forced through the capillary by air pressure measured by a suitable manometer, and the time taken to pass from mark m_3 to m_4 measured by a stop-watch reading to 0·2 second. Readings are then taken in the opposite limb and the two sets averaged. The traps

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T_1, T_2 provide a convenient means of readjusting the volume of liquid to its constant working value; the mean height of the constant volume thus secured, multiplied by the density at the working temperature, is added to the manometer pressure.
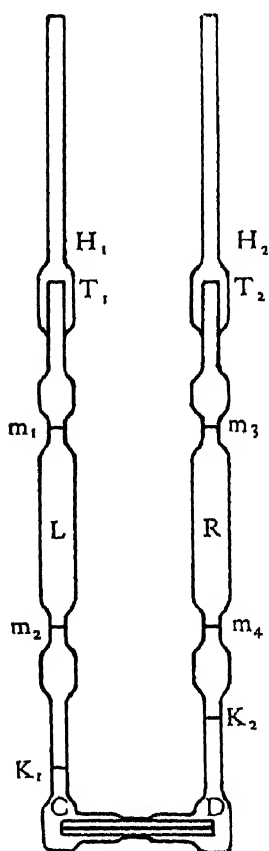
FIG. 9.—Thorpe and Rodger's viscometer.

Thorpe and Rodger observed the passage of the meniscus through the marks by means of a telescope, which could be moved vertically between suitable stops; this method has not been used since. The viscometer was immersed in a large tank provided with a jacket; tank and jacket were filled with water or glycerin, according to the range of temperature desired. No thermo-regulator was used, and the limits within which temperature fluctuated are not stated. The densities of the liquids at the various temperatures were calculated from data for their coefficients of expansion taken from the literature, or determined by Thorpe and collaborators.[1] The kinetic energy correction with $m = 1.00$ was applied to all determinations, but the λ correction was found unnecessary. The highest mean velocity was 66 cm./sec., which gives a Reynolds number considerably below the critical value for the lowest kinematic viscosity dealt with.

The diameter of the capillary at the two ends was determined by microscopic measurement before it was sealed in; it was redetermined afterwards by weighing with mercury, and the uniformity of the bore checked by measuring the length of a mercury thread in a number of positions. Alteration in the diameter of the capillary in consequence of the sealing in is avoided, cleaning facilitated, and risk of breakage reduced by a modification of the design used by Bingham and White [2] (fig. 10). In this instrument the capillary is not sealed but ground into two sockets; the vertical limbs

are similar in design to Thorpe and Rodger's, and in particular retain the traps for adjusting the volume. The three parts of the instrument are clamped in a metal framework, which keeps the joints between the capillary and the limbs tight.

A simpler instrument has been used for absolute determinations by Bingham and Jackson,[3] and is shown in fig. 11. It is filled by means of a pipette drawn out into a fine tube, and the liquid drawn into the left limb until it reaches from H to A, the excess overflowing into the trap. The left limb is then connected to a compressed-air receiver provided with a water manometer, and the time required by the meniscus to fall from B to D is taken; the right limb is then connected to pressure and the time from D to B is taken. The kinetic energy correction (6) is applied in full ($m = 1 \cdot 12$), but the λ correction is negligible with the dimensions used. It will easily be seen that equation (6) can be written:

FIG 10.—Bingham and White's viscometer

FIG 11.—Bingham and Jackson's viscometer.

$$\eta = C p t - C' \rho / t.$$

$C' = m Q / 8 \pi L$ can be calculated with sufficient accuracy from the known volume between marks and the length of the capillary; C is then found by observing the time t between marks for a liquid of known viscosity and density

at a given pressure:

$$C = \frac{\eta + C'\rho/t}{pt}.$$

The pressure requires further definition. The manometer reading is subject to small corrections, for which the original paper must be consulted. If the two bulbs were exactly equal, and at the same level, the hydrostatic head due to the differences in level at the beginning and end would cancel out; since this condition cannot be realised, there will be a small hydrostatic head, which will act in the same sense as the air pressure in one limb, and in the opposite sense in the other limb. The value of this correction can therefore be obtained by a simple elimination from the times of flow found for the right and the left limb, at constant air pressure and with a liquid of known constants. The sum, air pressure +hydrostatic head, thus found is, however, still not the mean effective pressure, which, with cylindrical bulbs of equal diameter, would be given by a formula with logarithmic terms similar to (9), p. 25. Bingham and Jackson, however, find that the difference between mean pressure and the applied pressure as defined above is negligible when the latter is more than thirty times the hydrostatic head due to the difference in level in the bulbs; as this should not exceed a few mm. in a reasonably well-made instrument, this condition can be easily satisfied.

Bingham and Jackson used the instrument to determine the viscosity of liquids which could be used as perfectly reproducible standards for calibrating viscometers. The use of such liquids is indispensable in viscometers such as the Ostwald instrument, when they are intended for determining viscosities considerably higher than that of water or readily available non-hygroscopic organic liquids; in tubes giving a reasonable time of flow for high viscosity, water would reach turbulent flow. Bingham and Jackson arrive at the conclusion, which has been very generally adopted, that the most suitable liquid is a solution of cane sugar. The complete table of viscosities at different concentrations and temperatures is given in Chapter VIII, p. 105.

(2) *Viscometers for Relative Viscosity* : (a) *Instruments with Variable Pressure.* It is obvious that Bingham and Jackson's instrument can be used for determining relative viscosities by the simple method described on p. 29 for Ubellohde's viscometer, provided the kinetic energy term is negligible; this point must be decided by testing the constancy of PT. The author is not aware of data on the accuracy obtainable with Ubellohde's instrument; it has been used in the investigation of colloidal solutions by Kirchof.[4]

(b) *Ostwald Viscometers.* The defects of the early form (fig. 6, p. 26) have already been discussed. Various modifications have been made by successive investigators to eliminate these sources of error. Jones and Veazey [5] used the form illustrated in fig. 12, in which the tube carrying the marks above and below the bulb is a wide capillary of uniform bore, so that the surface-tension effect is the same for the initial and terminal positions of the menis-
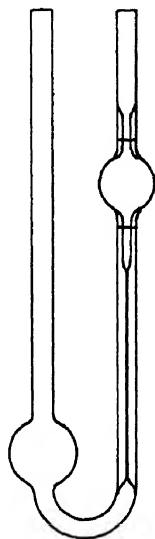
Fig. 12.—Jones and Veazey's viscometer.

cus. Applebey,[6] and Washburn and Williams,[7] designed viscometers with the special object of making all corrections unnecessary, and tested them by checking the constancy of PT for the whole range of velocity. Applebey accomplished this object by reducing the bore (R=0·2 mm.) without making it so small that occasional dust particles caused serious trouble ; by making the capillary long (11 to 22 cm.) and by reducing the hydrostatic head, *i.e.* placing the bulbs fairly close together: their minimum distance is fixed by the condition that the difference of level between the lower mark on the capillary and the surface of the liquid in the left-hand bulb must be greater than the capillary rise (fig. 13).

Fig. 13.—Applebey's viscometer.

Applebey used Grüneisen's method (*cf.* p. 29) for determining the mean hydrostatic head, and, like him, found it very approximately equal to the head at mean time. He then

tested the constancy of PT by means of the apparatus for maintaining a constant air pressure, shown in fig. 13A. The pressure in B was adjusted by forcing in air at E with a bicycle pump or letting it escape at D; A and B were made so large that the gauge reading did not fall more than 0·1 mm. as the bulb of the viscometer emptied itself.

Applebey found PT constant over the useful range of mean velocity, but considered the error in this method of testing to be greater than that in the viscosity determinations; he
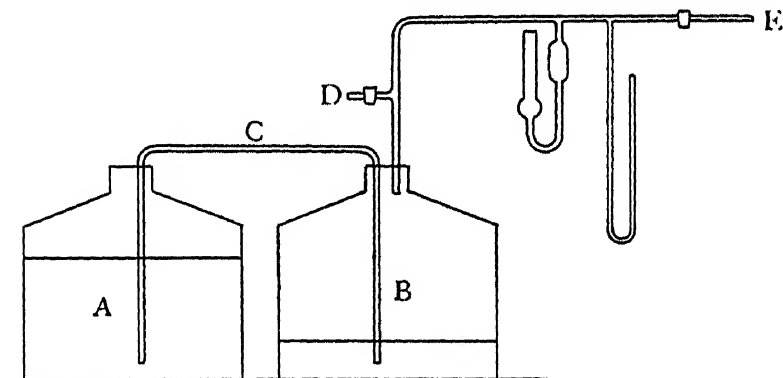
FIG. 13A.—Applebey's apparatus for testing constancy of PT.

found the kinetic energy correction unnecessary, a conclusion criticised by Bingham.[8]

Washburn and Williams's instrument is illustrated in fig. 14. The object of the design was not only to make all corrections unnecessary, but to eliminate certain minor troubles peculiar to glass instruments, such as alteration in the internal diameter due to the solvent action of cleaning fluids and water, contamination of the water by dissolved glass, and temperature hysteresis. The instrument was accordingly made of quartz; the dimensions of the capillary were: R=0·25 mm., L=19·5 cm.; capacity of the bulb 9 c.c. The large bulb was filled with a constant volume (60 c.c.) of liquid by a pipette. The constriction above the bulb was made of the same diameter as the capillary, so that the surface-tension effect is the same at both readings. The constancy of PT was checked by Applebey's method, and was found satisfactory without any kinetic energy correction;

the viscosities of, *e.g.*, water at different temperatures determined with the instrument were in excellent agreement with accepted data.

The upper portion of the instrument, which is not essential, prevents evaporation during the period of emptying. The two ends E and F are connected to the viscometer after it has been filled with the pipette, and the instrument is immersed in the thermostat so that the horizontal connection EF is covered; the three-way cock C is then turned to connect A with D, and the liquid is drawn into A by applying suction at D. When the liquid has risen above the constriction, the cock is closed and turned to connect E with F, when the reading is to be taken. The plan of connecting the two limbs to prevent evaporation has been adopted in several viscometers for volatile liquids (see below), and may cause errors due to the viscosity of the air displaced from one limb into the other, unless the rate of flow is small and the cross-section of the connections ample.

FIG. 14 —Washburn and Williams's viscometer.

The instruments just described are of somewhat special design, and the second of them requires a large volume of liquid. For the determination of relative viscosities with reasonable accuracy simpler types are generally adequate, provided they are standardised by careful determination of the time of flow for one or more accurately reproducible liquids of known viscosity and density, and that they are used for a range of kinematic viscosity not too far removed from that of the standardising liquid.

The British Engineering Standards Association in 1923

published drawings and specifications for four Ostwald visco-
meters suitable for kinematic viscosities (poises/density) from
0·009 to 15.   A new edition of these standards is in prepara-
tion, to which the reader is referred.

The necessary preliminary to the use of all capillary visco-
meters is careful cleaning of the instruments.   The most
generally used agent for this purpose is a mixture of equal
parts of concentrated sulphuric acid and of cold saturated
solution of potassium dichromate.   If possible, this should be
left in the viscometer overnight.   After cleaning with the
dichromate-sulphuric acid mixture and *copious* washing with
distilled water, the viscometer, either immediately or after
previous rinsing with filtered alcohol, must be dried by draw-
ing through it air which is filtered through cotton-wool before
entering the instrument.   Viscometers which are not filled
with liquid immediately after drying should be hung up
upside down.

Any thermostat which allows observation of the marks on
the viscometer and of the thermometer may be used, but for
accurate measurements a capacity of 30 to 50 litres is desirable.
The ordinary Ostwald toluene regulator will maintain tempera-
tures a few degrees above that of the room constant within
0·1° or even 0·05°, provided the mercury is clean and the
stirring effective.   The author prefers calcium chloride solu-
tion (10 to 20 per cent., as recommended by Ostwald-Luther)
to toluene, as it has a much smaller tendency to creep between
the glass and the mercury.   Whether constancy within 0·1°
is adequate must depend on the degree of accuracy desired,
and of course on the temperature coefficient of viscosity of the
liquid under examination.   The viscosity coefficient of water
decreases by about 2 per cent. per degree between 20° and 25°,
and that of a cane-sugar solution containing 60 grms. in 100
c.c. by about 4·4 per cent. per degree in the same interval.
Temperature fluctuation can be reduced to 0·02° or even
0·01° by the use of Lowry's [9] " fluted " or spiral regulator;
the fluted type is illustrated in fig. 15.   The gas enters at A
and passes to the burner at B; a small hole at C acts as by-
pass to keep the burner alight when the mercury cuts off the
supply.   Various other gas regulators and electric-heating

devices which reduce fluctuations to 0·01° have been described in the literature.[10]

Temperatures below that of the room are maintained by passing suitably cooled water through the thermostat and controlling the flow by a toluene regulator of the form illustrated in fig. 16. The column of mercury in *c* is so adjusted that the meniscus closes the overflow pipe *df* when the desired temperature is exceeded; while it is closed, the cooling water admitted at *h* passes into the thermostat at *g*. When the temperature has fallen sufficiently, the mercury uncovers the opening *d* and the cooling water runs to waste through *df*.

FIG. 15.—Lowry's gas regulator.

FIG. 16 —Regulator for cold water.

(c) *Capillary Viscometers for Special Purposes :* (1) *For Volatile Liquids.* Any ordinary Ostwald instrument can be transformed into one more or less protected from communication with the atmosphere by the addition of a connecting piece with two- or three-way cock, as used by Washburn and Williams (p. 45). The necessity of keeping all air passages large enough to avoid errors due to the viscosity of the air has already been pointed out. Similar errors are likely to be caused by the expedient sometimes adopted[11] of connecting the limbs of the instrument with bulbs containing cotton- or glass-wool moistened with the liquid under examination. A number of special viscometers have been described in the literature,[12] and may be useful when volatile liquids have to be constantly investigated;

a type proposed by Ostwald and Luther is illustrated in fig. 17. The large bulb is filled from *a*, the stopper having been removed; it is then replaced so that the opening at *e* is closed, the cocks *c* and *d* opened, and the liquid forced into the right-hand bulb by air admitted at *b*. The cocks *c* and *d* are then closed, and *a* turned to establish communication with *e*, when the bulb begins to empty.
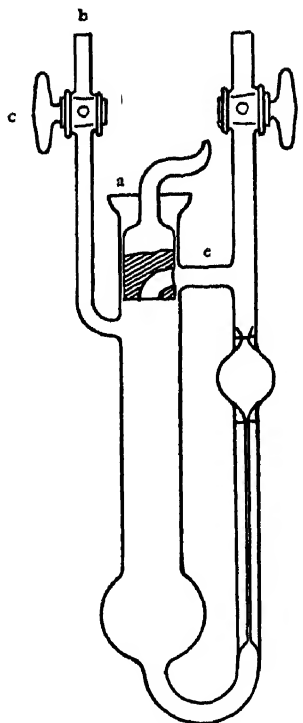
FIG. 17.—Ostwald viscometer for volatile liquids.

(2) *For Opaque Liquids.* For liquids so opaque that the passage of the meniscus through the marks cannot be seen, a modified Ostwald viscometer as illustrated in fig. 18 may be used.[13] The instrument is filled, the stop-cock being closed, so that the liquid almost fills the space from mark A to B; the volume is finally adjusted when the desired temperature has been reached. The cock is then opened, and the time taken by the liquid to pass from mark C to mark D is noted. As a repetition of the reading is not possible without cleaning out the instrument, care must be taken to ensure that the liquid in it has really assumed the temperature of the thermostat. The instrument is calibrated with a suitable liquid, and the results are calculated in the same way as with the ordinary Ostwald viscometer.

FIG. 18.—Ostwald viscometer for opaque liquids.

(3) *Viscometer with Filter.* An instrument designed for the

study of fused salts of low melting-point (up to 220°), which may be useful for other purposes, has quite recently been described by Walden, Ulich, and Birr.[14] They found that it was impossible, even with careful working, to get the fused substance into the instrument free from filter fibres, etc., and accordingly attached a small suction filter with a Schott porous glass plate to the bulb (fig. 19). The constant volume of 2 c.c. was secured by weighing into the funnel an amount of salt $=(2/\rho_t+a)$, ρ_t being the density of the substance at the temperature t at which the determinations were carried out, and a the constant volume retained in the pores of the filter plate. The instrument was then heated to t in an oil-bath and the fused salt drawn into the left-hand bulb by vacuum. The arrangement and use of the taps explain themselves.
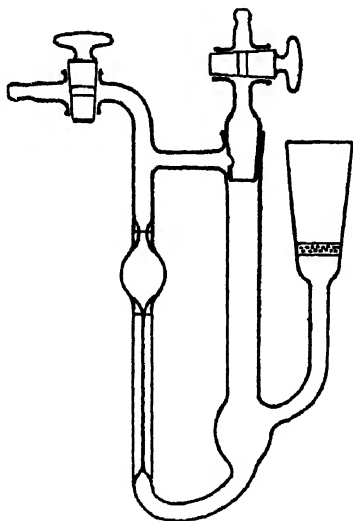
FIG. 19.—Ostwald viscometer with glass filter.

(d) *Viscometer with Porous Septum instead of Capillary.* J. Duclaux and J. Errera [15] point out that Ostwald viscometers calibrated with, or giving reasonable times of flow for, water and aqueous solutions are generally unsuitable for liquids of low viscosity like ether or hydrocarbons, the flow of which would become turbulent. To secure a reasonable time of discharge with a standardising liquid like water, and also laminar flow with limpid organic liquids, they suggest a large number of small capillaries in parallel; if a single tube is replaced by 10,000 tubes with a radius $\frac{1}{10}$ and a length $\frac{1}{100}$ that of the single tube, the time of efflux for a given volume will be reduced to $\frac{1}{100}$, while flow will be laminar at much lower kinematic viscosities. They replace the capillary by a filter candle as used in sterilising liquids (pores about 2μ diameter), which is luted to a tube provided with a bulb; marks and constrictions at a, a' define a constant volume (fig. 20). The liquid is drawn above a and the level in the outer vessel

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made up to *b*, where it is kept constant by the overflow into the bulb. The instrument is calibrated with a liquid of known viscosity and density, and the same formula applies to it as to the Ostwald viscometer.
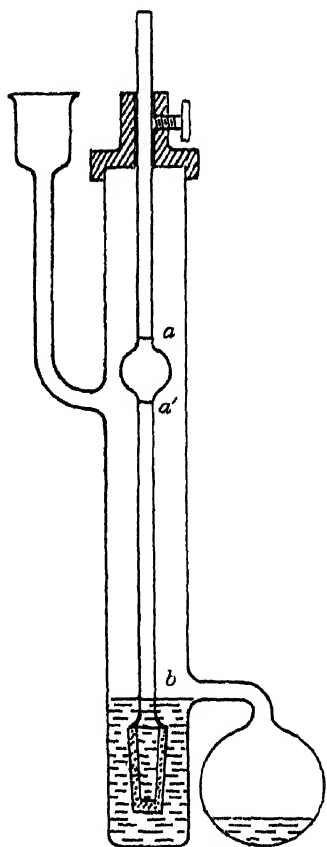
FIG. 20.—Porous cell viscometer.

As the pores in a ceramic material are neither circular in cross-section nor straight, there is no *a priori* reason for assuming that the flow through such a septum would conform to Poiseuille's Law; the authors consider that this conformity has been proved by E. Duclaux [16] and J. Brunhes,[17] and give the results of experiments made by themselves to prove (1) that the time of efflux for a given liquid and pressure is constant; (2) that the product PT is constant; and (3) that the relative viscosities (that of ether being taken as =1) are proportional to the times of efflux.

PT for ether and amyl alcohol is constant within less than 0·5 per cent. As regards (3), the statement cannot be checked by the data given by the authors. The time of efflux was taken with a constant pressure of 165·2 mm. of water; the variable head of liquid, *i.e.* the distance between the marks, is not stated, and the temperature is not given. As PT is constant for two liquids with such different viscosities as ether and amyl alcohol, it should be possible to get correct values of the relative viscosities.

B. Concentric Cylinder Apparatus. The equations developed in the preceding chapter apply strictly to a portion of an infinitely long cylinder, and the problem which has to be solved in the construction of apparatus is that of eliminating the effect of such ends as both cylinders must have. These

effects can be eliminated physically by protecting the ends of the inner cylinder with some form of guards which prevent the drag exerted by the bottom of the outer cylinder from being transmitted to the inner one; or they can be eliminated mathematically by using two different lengths of the inner cylinder, keeping the relative distance of the ends constant, and thus finding the additional length of cylinder which would produce the same couple as the bottom. The former method was adopted by Couette (*loc. cit.*, p. 13), who first investigated the concentric cylinder system experimentally, and has been followed by the author; [18] the latter was used by Gurney [19] in an investigation on the constancy of the viscosity coefficient at low velocity gradients, to which reference will be made

FIG. 21 —Couette's concentric cylinder apparatus.

again, and is employed in Searle's apparatus, to be described below.

Couette's apparatus, which has recently been copied without essential alterations by Leroux,[20] is shown in diagrammatic sectional elevation in fig. 21. The inner cylinder A is suspended from a wire B and centred by a pivot C. The outer cylinder D rests on the spindle E, and is rotated at constant speed. The effects of the bottom of D and of the liquid

surface are eliminated by the two guard cylinders F, F'; if this elimination is complete, the apparatus gives the simple relations deduced on p. 31, *i.e.* deflection plotted against angular velocity lies on a straight line passing through the origin, or deflection/angular velocity, plotted against the latter, falls on a straight line parallel to the axis of ω. Fig. 22 shows this graph for Couette's original apparatus; the onset of turbulence (dotted) is quite abrupt.

Couette used a pivot to prevent instability of the suspended cylinder, but no trouble from this cause has been experienced by later observers, like Mallock,[21] Gurney, and the author, who all dispensed with the pivot. The latter is undoubtedly a source of error; Couette found that the values for the viscosity of water determined after the apparatus had been standing still for a considerable time differed seriously from those found before this period of rest. The pivot friction is also certain to differ appreciably in liquids with different lubricating properties, so that it cannot be treated as a constant of the apparatus except for a given liquid.

FIG. 22.—Couette's graph : ord. θ/ω, absc. ω.

The author's modification of Couette's apparatus, which has been extensively used by him [22] as well as by Freundlich and his collaborators [23] in the study of colloidal solutions, is illustrated in its present form in fig. 23. The guards E, E' do not overlap the suspended cylinder A, but have edges bevelled under 45°, leaving a clearance of 2 mm. between them and parallel bevels on A; a plate H with a diameter 2 mm. smaller than that of the outer cylinder D provides further protection against the effect of the bottom. The deflection is read by mirror (G) with scale and telescope, and the whole system of suspended cylinder and guards is centred by means of the centring head at the top of the apparatus. The guard

cylinders are supported by three vertical rods fixed in the centring head, which pass through three circular slots in the suspended cylinder (see the small plan); this arrangement allows a deflection of about 100°, which is of course much in excess of what is required. The negligible error caused by small eccentricity—1 mm. with cylinders 10 and 11 cm. diameter—has been proved by Gurney. With these dimensions the linear relation between angular velocity and deflection holds up to about $\omega = 100°$ of arc per second for liquids with a kinematic viscosity equal to, or greater than, that of water.

With this and other concentric cylinder apparatus, temperature control, or rather the use of widely varying temperatures, is difficult; temperatures differing little from that of the room

FIG. 23.—Hatschek's concentric cylinder apparatus

are, however, easily maintained for sufficient periods when the outer cylinder is lagged with non-conducting material. The author has lately adopted the plan of enclosing the whole apparatus in a wooden chamber, which is fitted with an

electric heater and thermo-regulator, as well as with a small electric fan for maintaining circulation.

In Searle's apparatus [24] the outer cylinder is fixed, while the inner is rotated. The deduction given on p. 30 applies equally to this arrangement, and if G is the couple (dyne-cm.) which maintains a constant speed equivalent to one revolution in T seconds, the viscosity coefficient is

$$\eta = \frac{GT(R_2{}^2 - R_1{}^2)}{8\pi^2 R_1{}^2 R_2{}^2 L} = K\frac{GT}{L}.$$

The inner cylinder (fig. 24) is carried by a spindle working

FIG. 24.—Searle's concentric cylinder apparatus.

in fixed bearings, the lower one being provided in the top of the pillar which supports the outer cylinder. The couple G is produced by two masses, each of M grm., carried by threads wound round a drum on the axle and passing over ball-bearing pulleys. Above the drum is a plate bearing a mark whose passage past a pointer shows when each revolution is complete. A locking pin enables the inner cylinder to be arrested.

If the effective diameter of the drum (diameter of metal + diameter of thread) is D cm., then $G = g$MD (g = gravity constant) and

$$\eta = KgD\frac{MT}{L}.$$

As has been explained, the formula applies to a length L of an infinite cylinder, and, to make it applicable, the end effect must be eliminated, which can be done by exposing different lengths of the inner cylinder to the viscous drag of the liquid. The outer cylinder can be moved vertically for this purpose, and clamped in a fixed position by a clamp acting on the tube projecting from its bottom. A scale of mm. is engraved on the inner cylinder, on which the level of the liquid can be read through a narrow slot in the outer cylinder,

covered by a glass plate cemented to it and secured by a brass plate. By raising or lowering the outer cylinder the length L can be altered; a perforated plate, loosely fitting the outer cylinder and fixed to the top of the pillar, prevents the liquid from being disturbed when the inner cylinder revolves, so that the conditions at the lower end of the rotating cylinder remain unaltered when the level of the liquid is varied. Hence, if L is the immersed length of the inner cylinder, the couple required to maintain a given angular velocity will (if L is not too small) be proportional to L+l, where l is the correction for the end effect, which can be deduced from two sets of observations. The formula then becomes:

$$\eta = KgD\frac{MT}{L+l}.$$

For a given η and L, the product MT must therefore be a constant, and this condition can be used for checking the correct working of the apparatus, by plotting $1/T$ against M, when a straight line passing through the origin should result. Lewis [25] has examined certain anomalous results obtained by Molin [26] with syrup, and finds that the $1/T$-M graphs for all values of L are straight lines which, however, do not pass through the origin, but through the same point on the positive side of the axis of M. This means that a certain couple must be applied before the cylinder begins to revolve, the mass necessary to produce it (for the particular apparatus used) being the intercept on the M-axis. This friction would differ with different liquids, as both the effective weight of the inner cylinder and the coefficient of friction at the bearing would vary.

C. Falling Sphere Viscometers. Two practical considerations limit the application of this method to liquids of high viscosity: the most readily obtainable exact spheres of small diameter are the steel balls used for ball bearings, with a density of about 7·6, and the maximum velocity of fall at which the passage through two marks can be accurately timed, which is generally put at 1 cm. per second. The smallest current size is 0·15 cm. diameter, accurate within 0·0025 cm., i.e. 0·16 per cent. The viscosity of a liquid with

a density $=1$, in which such a ball falls with a velocity of I cm. per second—assuming an infinitely extended liquid— is 8·24 poises. In practice the ball is allowed to fall in the axis of a tube conforming to Laden-burg's criteria (p. 35), and the viscosity calculated from his formula; alterna-tively the apparatus can be calibrated with a liquid of known viscosity η_1 and density ρ_1, for which the time of fall between the marks has been found to be t_1. If the time for a second liquid of density ρ_2 is t_2, and ρ is the density of the ball, the viscosity of the second liquid is

$$\eta_2 = \eta_1 \frac{(\rho - \rho_2)t_2}{(\rho - \rho_1)t_1}.$$

No easily reproducible liquid of suffi-ciently high viscosity is available for calibration; the viscosities of glycerin and of castor oil are of the right order, but the former varies considerably with very small variations in the water content, while castor oil is not suffi-ciently definite. It will therefore be generally necessary to make a careful determination of the absolute viscosity of the calibrating liquid in a suitable capillary viscometer.

FIG. 25.—Falling sphere viscometer. (Gibson and Jacobs.)

A simple form of apparatus has been used by Gibson and Jacobs [27] for the study of cellulose nitrate solutions (fig. 25). The fall tube has an internal diameter of 2 ± 0.05 cm. and a total length of 29 cm.; it carries five marks at distances of 5 cm. The sphere, a steel ball of 0·15 cm. diameter, is dropped in through a tube of 3 mm. internal diameter, fixed centrally in the stopper and provided with a small hole above the level of the liquid; the lower end of this tube is level with the first mark, and the liquid stands 3 cm. above

it. The time of fall between the second and fifth marks (=15 cm.) is taken with a stop-watch. The authors do not describe the method of sighting, but if the marks are carried round the whole circumference and the liquid is sufficiently transparent, this can probably be done without parallax even without the use of a telescope. The tube is enclosed in a large cylinder fitted with thermometer and stirrer. The authors tested the apparatus with castor oil and obtained a value in close agreement with those in the literature—9·88 poises at 20°.

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CHAPTER IV

THE CONSTANCY OF THE VISCOSITY COEFFICIENT

THE viscosity coefficient has been defined as the force required per unit area to maintain unit velocity gradient (p. 5). This definition contains the assumption that the coefficient is independent of the velocity gradient, and it has accordingly been treated as a constant in the differential equations deduced in Chapter II.

It is necessary to point out that this assumption is a purely *a priori* one and requires proof, a considerable measure of which is, of course, to be found in the fact that the equations deduced for the flow through a capillary tube or the moment in the concentric cylinder apparatus agree with experience. The product PT, for instance, could not be constant for a given capillary if the viscosity coefficient varied with the velocity gradient and therefore with the pressure. The constancy of this product has been checked many times, although very generally only for water, and over a range of velocity gradient to which the onset of turbulence sets an upper limit. There is, on the other hand, no lower limit at which Poiseuille's Law ceases to hold, and it is therefore possible to use extremely low velocity gradients, and to ascertain whether the viscosity coefficient of a given liquid remains unaltered.

The maximum velocity gradient in a capillary is (p. 17)

$$\frac{dv}{dr} = \frac{PR}{2L\eta},$$

where R is the radius of the capillary. To obtain a numerical value for ordinary working conditions, we may take as

example Washburn and Williams's instrument (p. 45) and water at 20°:

$$R = 0 \cdot 025 \text{ cm.}; \quad L = 19 \cdot 5 \text{ cm.}; \quad P = 20 \times 981 \text{ dynes/cm.}^2;$$
$$\eta = 0 \cdot 01.$$

The maximum velocity gradient is accordingly 1258 cm. per second per cm. The capillary in this instrument is of small bore and unusual length, and much higher velocity gradients are common without the region of turbulence being reached.

The first investigation with the object of determining the viscosity coefficient of a liquid at very much lower velocity gradients than are usual was carried out by Duff,[1] who examined water and "a heavy kerosene." The capillary was 139·5 cm. long, with a mean radius of 0·1675 cm.; it connected two large beakers, the level of liquid in which was measured by optical levers actuated by floats. The initial difference in level necessary to cause flow through the tube was established by rapidly letting out liquid from one beaker or by lowering a solid body into it. The tube was calibrated by a mercury column of eighteen steps, and the radii thus determined showed a maximum deviation from the mean of 1·4 per cent., and a mean deviation from the mean of 0·7 per cent., while the difference of the maximum and minimum diameter at the two ends did not exceed 1 per cent. The viscosity coefficient was calculated by formula (9), p. 25, with the modification necessary to allow for a difference in cross-section of the two beakers. The whole apparatus was immersed in a large water-bath placed in a constant temperature room.

The difference in level was kept so small that the maximum velocity gradient for water was about 5 cm./sec./cm., and about 0·2 cm./sec./cm. for kerosene. In successive experiments the following values of the viscosity coefficient of kerosene were obtained at this gradient, the values in brackets having been determined at a velocity gradient of 20,000 cm./sec./cm.:

0·0232 (0·0235);　0·0243 (0·0235);　0·0239 (0·0239);
0·0244 (0·0244).

The coefficient is therefore independent of the velocity gradient within these limits.

The results with water varied according to the time the water had been in the apparatus, the viscosity increasing with time.   Duff came to the conclusion that this variation was caused by dissolved glass (the tube was made of ordinary German soda glass) with the possible formation of colloidal silica.   When the tube was "lightly silvered" the variation with time ceased to show itself.   Duff found finally that the viscosity coefficient of water was constant within a range of velocity gradient from about 5 cm./sec./cm. to 500,000 cm./sec./cm.

The next investigation by Gurney [2] is of interest as being one of the few absolute determinations carried out in the concentric cylinder apparatus.   The end effect was eliminated by using two internal cylinders of the same diameter but different lengths; apart from this, the apparatus was used as described (p. 53).   With the diameters chosen by Gurney (11 : 10) the velocity gradient is approximately linear, and the average velocity gradients, as well as the viscosity co-efficients found at them, are given below.

Velocity gradient (cm /sec./cm).	η (Centip.).
5·287	0·9319 (at 21°)
1·287	0·9306 (at 24°)
0·663	1·0013 (at 21°)

Gurney compares these figures with values interpolated from Landolt and Börnstein's tables, and finds them respectively 0·8, 0·7, and 0·9 per cent. too high; the discrepancy between them and Bingham and Jackson's interpolated figures (Table IA) is greater, and for the third set amounts to 2 per cent.   Gurney considers that the most probable cause of the divergence is a deviation from truly circular and uniform section in his cylinders, and concludes that his measurements "do not justify the claim that the viscosity of water is higher at these low velocity gradients.   But they justify the counter-claim that it is not more than 1 per cent. greater, if at all."

To verify Duff's results, Gurney also measured the viscosity of water saturated with glass by standing over glass powder for a week, but could find no difference between this and pure water exceeding the experimental error.

A modification of Duff's method was used by Griffiths and Knowles.[3] Griffiths had previously proved that the gradual increase in viscosity of water which had remained in the tube for some time was quite real, but was due to some organic growth, which could be prevented by the addition of one drop of 20 per cent. copper nitrate solution to one litre of (air-free distilled) water. This, by the way, agrees well with Duff's observation that the water in the silvered tube remained unchanged: a thin silver mirror would not be sufficiently coherent to protect the glass, but the well-known "oligo-dynamic" * action of silver in a very small volume of water would effectively prevent the growth of any organisms. In Griffiths and Knowles's apparatus the volume passed through the capillary (0·0292 cm. radius and 130·175 cm. long) was determined by measuring from time to time the distance travelled by a coloured index of uranine solution introduced into the column of water in the capillary, a method described by Griffiths in an earlier paper.[4] The maximum velocity gradient used was 1 cm./sec./cm., and the viscosity coefficient at 16·03° was found =1·119 cp. as the mean of four determinations, which is in good agreement with Bingham and Jackson's interpolated value for 16°, viz. 1·111.

The author is not aware of other investigations at very low velocity gradients, but those just summarised prove conclusively that the viscosity coefficient of, at all events, water is a real constant at constant temperature. It is perhaps to be regretted that no liquid with properties less anomalous than those of water has been studied in the same way, though there appears to be no reason for doubt that the result would be the same.

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* The term was invented by Naegeli to describe the inhibiting effect on organic growth of metals in concentrations far below those which can be detected by the usual reactions (*e.g.* inhibition of algal growths in water kept in clean copper vessels).

CHAPTER V

THE VARIATION OF VISCOSITY WITH TEMPERATURE

THE viscosity of all liquids and solutions decreases with rising temperature. It was known already to the hydraulic engineers of the late eighteenth and early nineteenth century that the flow of water in pipes, other things being equal, increased with rising temperature. Hagen (*loc. cit.*, p. 10) investigated the volume of water discharged through capillaries at different temperatures and found an increase with rising temperature, as well as a tendency to deviations from the law he had found —deviations which we now know to be caused by the earlier onset of turbulence, brought about by the lower (kinematic) viscosity at higher temperatures.

Empirical Formulæ. The first quantitative investigations were carried out by Poiseuille (*loc. cit.*, p. 10). He found that the viscosity η_t of water at the temperature t could be expressed in terms of the viscosity η_0 at 0°, and the temperature by the empirical formula

$$\eta_t = \frac{\eta_0}{1 + at + \beta t^2} \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

Koch (*loc. cit.*, p. 25) found that the viscosity of mercury could be expressed for the temperature interval from $-21\cdot4°$ to $+340°$ by an equation containing a cubical term:

$$\eta_t = 0\cdot016969 - 0\cdot0_4660525t + 0\cdot0_520847t^2 - 0\cdot0_92455t^3 \quad (2)$$

A number of other empirical formulæ has been proposed by various authors. For small temperature intervals Meyer [1] finds the quadratic term in equation (1) unnecessary, so that

it becomes :

$$\eta_t = \frac{\eta_0}{1 + at} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

The η-t curves for water (temperature scale on lower axis) and mercury (temperature scale on upper axis) are shown in
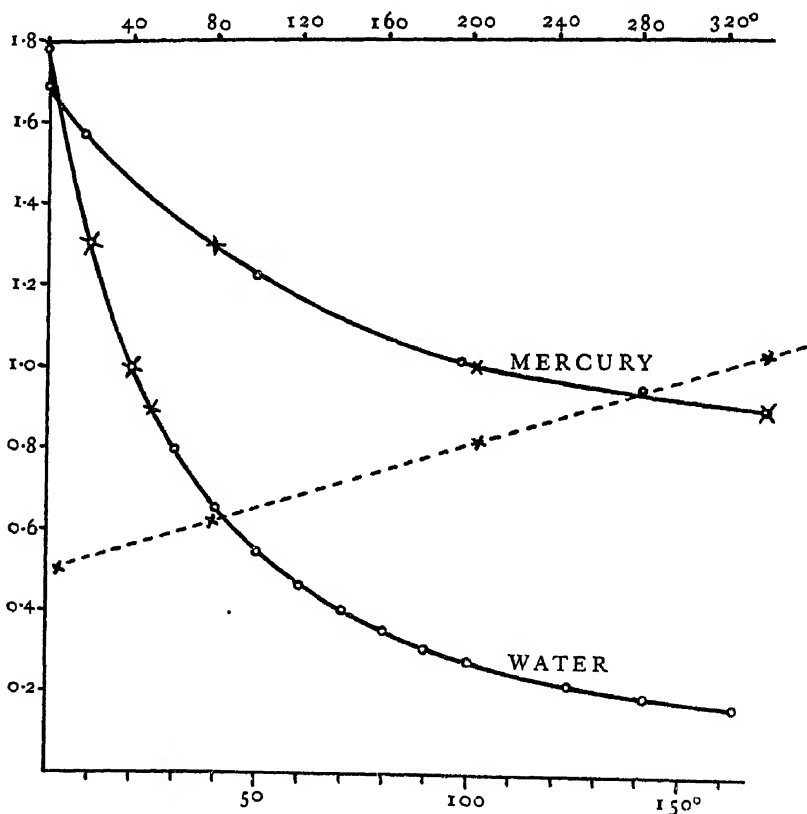
FIG. 26.—Viscosity-temperature curves of water (lower scale) and mercury (upper scale). The dotted line shows Porter's relation (see p. 74).

fig. 26; the scale of η is the same for both. The values for water below the boiling-point are due to Thorpe and Rodger, the three values above 100° to de Haas,[2] while the values for mercury are Koch's.

Graetz [3] has deduced a formula from theoretical considerations which contains the critical constants of the liquid. For

temperatures far removed from the critical it simplifies to

$$\eta_t = A\frac{t_c - t}{t - t_1} \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

in which A is a constant, t_c the critical temperature, and t_1 a temperature well below the freezing-point of the liquid, which, for all practical purposes, is a second constant to be determined from the experimental data. The formula fits the η-t curves of a large number of liquids, including a number of those investigated by Thorpe and Rodger, but fails with others.

Slotte [4] has proposed several empirical formulæ, one of which,

$$\eta = \frac{C}{(a + t)^n} \qquad . \qquad . \qquad . \qquad . \qquad (5)$$

has been applied by Thorpe and Rodger to all their measurements—which it represents, on the whole, with very good agreement. The three constants, C, a, and n, for a few liquids investigated by them are tabulated below.

	C.	a.	n.
Water (5·47° to boiling-point) .	5·9849	43·252	1·5423
Pentane	19·459	165·59	1·7295
Chloroform	70·4244	158·33	1·8196
Ethyl ether	3·8307	136·38	1·4644
Ethyl alcohol . . .	251908000	209·63	4·3731

Comparison between these figures is obviously impossible. In looking for regularities in homologous series, Thorpe and Rodger accordingly tried the formula (5) with the denominator expanded as far as the third term, in the form

$$\eta_t = \frac{C}{1 + \alpha t + \beta t^2}.$$

Table I gives the viscosities at 20° of a number of organic liquids, and the coefficients α, β, and C. Table IA gives the viscosity of water at intervals of 5°, and the viscosity at every degree, calculated by Bingham and Jackson by

formula (12) (p. 74), from weighted averages of a number of determinations by various observers.

TABLE I

VISCOSITY COEFFICIENTS OF ORGANIC LIQUIDS AT 20° (CENTIP.), AND COEFFICIENTS IN INTERPOLATION FORMULA $\eta_t = \dfrac{C}{1 + at + \beta t^2}$ (THORPE and RODGER)

Substance.	η_{20}.	a.	β.	C.
Pentane	0·232	0·01044	$0·0_2301$	0·002827
Hexane	0·320	0·01122	$0·0_3337$	0·003965
Heptane	0·4105	0·01214	$0·0_4004$	0·005180
Octane	0·538	0·01394	$0·0_4926$	0·007025
Isopentane . . .	0·223	0·01088	$0·0_41331$	0·002724
Isohexane . . .	0·300	0·01110	$0·0_3509$	0·003713
Isoheptane . . .	0·379	0·01199	$0·0_3863$	0·004767
Methyl sulphide . .	0·293	0·00997	$0·0_41584$	0·003538
Ethyl sulphide . .	0·4445	0·01219	$0·0_3340$	0·005589
Thiophen . . .	0·659	0·01518	$0·0_4358$	0·008708
Carbon disulphide .	0·367	0·00820	$0·0_41302$	0·004294
Acetaldehyde . . .	0·2215	0·00963	$0·0_2953$	0·002671
Dimethyl ketone . .	0·3225	0·01064	$0·0_3115$	0·003949
Methyl-ethyl ketone .	0·423	0·01284	$0·0_3639$	0·005383
Diethyl ketone . .	0·4655	0·01270	$0·0_3734$	0·005949
Methyl-propyl ketone .	0·501	0·01325	$0·0_3965$	0·006464
Acids : Formic . .	1·782	0·02870	$0·0_31695$	0·029280
Acetic . .	1·219	0·01826	$0·0_48537$	0·016867
Propionic . .	1·099	0·01720	$0·0_46941$	0·015199
Butyric . .	1·538	0·02109	$0·0_311073$	0·022747
Isobutyric .	1·315	0·01917	$0·0_49215$	0·018872
Anhydrides : Acetic .	0·902	0·01735	$0·0_46122$	0·012416
Propionic	1·116	0·02005	$0·0_48315$	0·016071
Isoprene	0·2155	0·01002	$0·0_41542$	0·002600
Diallyl	0·274	0·01118	$0·0_3017$	0·003388
β-Isoamylene . .	0·2115			
Methyl iodide . .	0·487	0·01067	$0·0_41719$	0·005940
Ethyl iodide . .	0·583	0·01113	$0·0_42658$	0·007190
Propyl iodide . .	0·737	0·01278	$0·0_3493$	0·009372
Isopropyl iodide . .	0·690	0·01277	$0·0_3899$	0·008783
Isobutyl iodide . .	0·870	0·01523	$0·0_4600$	0·011620
Allyl iodide . . .	0·7265	0·01316	$0·0_43341$	0·009296

TABLE I—*continued*

Substance.	η_{20}.	α.	β.	C.
Ethyl bromide　.　.	0·392	0·01064	0·0$_4$1822	0·004776
Propyl bromide　.　.	0·517	0·01174	0·0$_4$3121	0·006448
Isopropyl bromide　.	0·482	0·01193	0·0$_4$3588	0·006044
Isobutyl bromide　.　.	0·638	0·01333	0·0$_4$4762	0·008234
Allyl bromide .　.　.	0·4955	0·01177	0·0$_4$2871	0·006190
Ethylene bromide　.　.	1·716	0·02007	0·0$_4$7018	0·024579
Propylene bromide　.	1·619	0·01924	0·0$_4$7668	0·023005
Isobutylene bromide　.	2·169	0·02379	0·0$_3$1257	0·033209
Acetylene bromide　.	0·959	0·01339	0·0$_4$2999	0·012307
Bromine .　.　.　.	0·9935			
Propyl chloride　.　.	0·352	0·01104	0·0$_4$3381	0·004349
Isopropyl chloride　.	0·322	0·01185	0·0$_4$2580	0·004012
Isobutyl chloride　.　.	0·4565	0·01318	0·0$_4$4045	0·005842
Allyl chloride .　.　.	0·3295	0·01111	0·0$_4$2639	0·004059
Ethylene chloride　.　.	0·833	0·01653	0·0$_4$5451	0·011269
Methylene dichloride　.	0·4355	0·01118	0·0$_4$1866	0·005357
Chloroform　.　.　.	0·564	0·01149 ·	0·0$_4$2588	0·007006
Carbon tetrachloride　.	0·969	0·01801	0·0$_4$6747	0·013466
Carbon dichloride　.	0·8925	0·01294	0·0$_4$3243	0·01139
Benzene .　.　.　.	0·649	0·01861	0·0$_4$6181	0·009055
Toluene .　.　.　.	0·586	0·01462	0·0$_4$4220	0·007684
Ethyl benzene .　.　.	0·665	0·01448	0·0$_4$4530	0·008745
Ortho-xylene　.　.　.	0·807	0·01701	0·0$_4$5636	0·011029
Meta-xylene　.　.　.	0·615	0·01418	0·0$_4$3923	0·008019
Para-xylene　.　.　.	0·6435	0·01472	0·0$_4$4578	0·008457
Methyl alcohol　.　.	0·591			
Ethyl alcohol .　.　.	1·192			
Propyl alcohol .　.　.	2·255			
Butyl alcohol .　.　.	2·947			
Allyl alcohol　.　.　.	1·361			
Isopropyl alcohol　.　.	2·369			
Isobutyl alcohol　.　.	3·906			
No 1. Inactive amyl alcohol	4·396			
No. 2. Inactive amyl alcohol	4·341			
Active amyl alcohol .　.	5·091			
Dimethyl ethyl carbinol　.	4·642			

[TABLE Ia

TABLE Ia

VISCOSITY OF WATER IN CENTIPOISES

(THORPE and RODGER and BINGHAM and JACKSON)

Temp.	T. and R.	B. and J.	Temp.	T. and R.	B. and J.	Temp.	T. and R.	B. and J.
0	1.7766	1.7921	35	0.7190	0.7225	70	0.4048	0.4061
1		1.7313	36		0.7085	71		0.4006
2		1.6728	37		0.6947	72		0.3952
3		1.6191	38		0.6814	73		0.3900
4		1.5674	39		0.6685	74		0.3849
5	1.5083	1.5188	40	0.6525	0.6560	75	0.3782	0.3799
6		1.4728	41		0.6439	76		0.3750
7		1.4284	42		0.6321	77		0.3702
8		1.3860	43		0.6207	78		0.3655
9		1.3462	44		0.6097	79		0.3610
10	1.3014	1.3077	45	0.5959	0.5988	80	0.3547	0.3565
11		1.2713	46		0.5883	81		0.3521
12		1.2363	47		0.5782	82		0.3478
13		1.2028	48		0.5683	83		0.3436
14		1.1709	49		0.5588	84		0.3395
15	1.1324	1.1404	50	0.5464	0.5494	85	0.3336	0.3355
16		1.1111	51		0.5404	86		0.3315
17		1.0828	52		0.5315	87		0.3276
18		1.0559	53		0.5229	88		0.3239
19		1.0299	54		0.5146	89		0.3202
20	1.0005	1.0050	55	0.5044	0.5064	90	0.3140	0.3165
21		0.9810	56		0.4985	91		0.3130
22		0.9579	57		0.4907	92		0.3095
23		0.9358	58		0.4832	93		0.3060
24		0.9142	59		0.4759	94		0.3027
25	0.8900	0.8937	60	0.4676	0.4688	95	0.2970	0.2994
26		0.8737	61		0.4618	96		0.2962
27		0.8545	62		0.4550	97		0.2930
28		0.8360	63		0.4483	98		0.2899
29		0.8180	64		0.4418	99		0.2868
30	0.7965	0.8007	65	0.4343	0.4355	100	0.2814	0.2838
31		0.7840	66		0.4293			
32		0.7679	67		0.4233			
33		0.7523	68		0.4174			
34		0.7371	69		0.4117			

Table II gives the coefficients of expansion of a few of the organic liquids, i.e. the coefficients a, b, and c in the equation

$$V_t = V_0(1 + at + bt^2 + ct^3) \qquad . \qquad . \qquad . \qquad (6)$$

TABLE II

COEFFICIENTS OF EXPANSION OF LIQUIDS (THORPE and RODGER)

$$V_t = V_0(1 + at + bt^2 + ct^3)$$

Liquid.	$a.$	$b.$	$c.$
Pentane . . .	$0·0_214646$	$0·0_530932$	$0·0_716084$
Hexane . . .	$0·0_212665$	$0·0_517113$	$0·0_712315$
Octane . . .	$0·0_211830$	$0·0_618665$	$0·0_712947$
Methyl iodide . .	$0·0_21444$	$0·0_540465$	$0·0_727393$
Propyl iodide . .	$0·0_210276$	$0·0_518658$	$0·0_{10}508$
Ethyl bromide . .	$0·0_213376$	$0·0_515013$	$0·0_7169$
Propyl bromide . .	$0·0_212239$	$0·0_656696$	$0·0_71369$
Methyl sulphide . .	$0·0_213260$	$0·0_521302$	$0·0_72329$
Ethyl sulphide . .	$0·0_211964$	$0·0_518065$	$0·0_87882$
Benzene . . .	$0·0_211762$	$0·0_512775$	$0·0_880648$
Para-xylene . .	$0·0_397013$	$0·0_68714$	$0·0_85287$
Ethyl alcohol . .	$0·0_210414$	$0·0_67836$	$0·0_717618$
Propyl alcohol . .	$0·0_374601$	$0·0_549478$	$0·0_713929$

As Thorpe and Rodger's results have been widely used, a brief discussion of their accuracy seems of interest. They estimate the probable error in their measurements as being of the order of 1/5000 (= 0·02 per cent.). Even if this figure is accepted, it must be remembered that they used the kinetic energy correction with factor $m = 1$, and that it amounts to 3 to 4 per cent. of the value found experimentally. If m is taken as $= 1·12$ (the value generally used, e.g., by Bingham), the corresponding corrections become 3·36 to 4·48 per cent.; in other words, the possible error caused by the uncertainty regarding m amounts to 0·36 to 0·48 per cent., and may affect the third figure.

Formulæ more complicated than Slotte's have been proposed by Duff,[5] and an expansion of Graetz's formula has been put forward by Brillouin.[6] It has been pointed out by Herschel [7] that two further formulæ, proposed respectively

by Batschinski [8] and by Dorsey,[9] are special cases of Slotte's formula, if this is written as follows:—

$$\eta_t = \frac{K}{(t-A)^n} \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

For $A = -273$ and $n = 3$, the formula becomes Batschinski's, *i.e.* the viscosity is inversely proportional to the cube of the absolute temperature; the agreement with experimental data is moderate only for many liquids. For $n = 1$ and A "the apparent temperature of solidification," the formula becomes one proposed by Dorsey.

McLeod's Theory. When Thorpe and Rodger's results in Tables I and II are considered, a certain connection between the viscosity and its temperature coefficient on the one hand, and the coefficients of expansion on the other, becomes obvious. In any homologous series the viscosity increases with the number of CH_2 groups, and the coefficients of expansion decrease; iso-compounds have a lower viscosity than the corresponding normal compounds, and their coefficients of expansion are higher. McLeod, who calls attention to these regularities, has attempted, with a fair measure of success, to establish a connection between the viscosity and the co-efficient of expansion.[10] He assumes that the viscosity is determined chiefly by two factors: one depending on the molecule itself, which, in unassociated liquids, is supposed to be independent of the temperature, and another depending on the free space within the liquid.

If η_t is the viscosity at the temperature t, and x_t the free space in unit volume at the same temperature, the function connecting them is assumed to be

$$\eta_t x_t^A = \text{const.} . \qquad . \qquad . \qquad . \qquad (8)$$

It can then be shown from experimental data that A is approximately unity for normal liquids, so that the viscosity is inversely as the free space.

If x_0 is the free space at $0°$, and α, β, and γ are the co-efficients of expansion, the free space x_t at the temperature t, assuming the expansion to be wholly confined to it and the

volume of the molecules to remain constant, will be

$$x_t = x_0 + \alpha t + \beta t^2 + \gamma t^3.$$

The ratio of the viscosities at $0°$ and $t°$ will then be

$$\frac{\eta_0}{\eta_t} = \left(\frac{x_0 + \alpha t + \beta t^2 + \gamma t^3}{x_0}\right)^A \qquad . \qquad . \qquad (9)$$

The two unknowns, x_0 and A, are determined by approximation, values being given to x_0 so as to make A have the same value for two temperature intervals, $t_0 - t_1$ and $t_0 - t_2$.

The formula gives notably better agreement with experimental results than those used by Thorpe and Rodger; in some cases (e.g. butyl alcohol), in which they had to use two or three sets of constants to cover the whole temperature range, one set of values of x_0 and A does so satisfactorily.

Table III is calculated from Thorpe and Rodger's results for viscosity and expansion. The first column gives the free space in unit volume at $0°$, and the third column the exponent A; the second column the free space at boiling-point, to which reference will be made below. Column 4 gives the temperature " furthest removed from those from which the constants were determined," and columns 5 and 6 the observed and calculated viscosities at these temperatures, which should show the maximum discrepancies.

McLeod summarises the results contained in Table III as follows. The free space in a homologous series decreases with increasing molecular weight, and the viscosity increases, as it should do, if it is a function of free space. That the free space decreases is also proved by the increase in density as a homologous series is ascended; the average weight of atoms added with each CH_2 group is about the same as that of the atoms in the preceding member, yet the density increases, so that the free space must be considered to have decreased.

The free space in iso-compounds at $0°$ is greater than in normal compounds, which agrees with the known facts that their densities and viscosities are lower than those of the normal compounds.

The free space at the boiling-point is practically the same for the majority of liquids examined, between $0·19$ and $0·21$.

A free space of 0·21 agrees fairly well with that calculated from the volume at boiling-point, which is 0·38 × critical volume for most liquids, provided that b is taken as 0·30 v_c (between van der Waals's figure, $b = v_c/3$, and the figure suggested by Berthelot, $b = v_c/4$).

TABLE III

FREE SPACE AT 0° AND AT BOILING-POINT (McLEOD)

Substance.	(1). x per unit volume at 0°.	(2). x at boiling-point.	(3). A.	(4). T°.	(5). η (obs.).	(6). η (calc.).
Hexane	0·1240	0·203	1·121	50	0·241	0·241
Heptane	0·1052	0·205	1·1225	70	0·253	0·253
Octane	0·0940	0·230	1·198	120	0·2075	0·2070
Iso-hexane	0·1260	0·202	1·055	50	0·2255	0·2270
Formic acid	0·0492	0·146	1·2785	80	0·682	0·684
Acetic acid	0·0988	0·202	1·8325	80	0·560	0·5595
Propionic acid	0·0727	0·212	1·245	80	0·5445	0·5436
Ethyl iodide	0·1153	0·189	1·145	50	0·444	0·445
Propyl iodide	0·0880	0·189	1·1065	80	0·4195	0·4191
Iso-propyl iodide	0·0955	0·189	1·139	60	0·463	0·463
Di-methyl ketone	0·1430	0·210	1·1187	40	0·268	0·268
Methyl-ethyl ketone	0·0960	0·191	1·037	60	0·2845	0·2835
Ethyl acetate	0·0853	0·181	0·9425	70	0·270	0·268
Propyl acetate	0·0830	0·200	1·124	80	0·3035	0·3020
Methyl alcohol	0·1037	0·171	1·5595	20 / 50	0·591 / 0·396	0·592 / 0·395
Ethyl alcohol	0·09215	0·172	1·948	20 / 50	1·192 / 0·6975	1·182 / 0·699
Propyl alcohol	0·0333	0·141	1·3237	30 / 70	1·7775 / 0·757	1·760 / 0·757
Iso-propyl alcohol	0·0559	0·145	2·104	20 / 60	2·37 / 0·804	2·31 / 0·817
Butyl alcohol	0·0563	0·168	2·085	110	0·4545	0·4524
Iso-butyl alcohol	0·0964	0·194	3·405	80	0·779	0·786

The exponent A is about 1 for a large number of sub-

stances, but assumes higher values for the fatty acids and also for the alcohols, rising to 3·405 for iso-butyl alcohol. All these liquids are known to be associated, and the association increases with falling temperature. The complexes of associated molecules enclose within them some of the space previously available as free space, so that the increase in viscosity on cooling is greater than is accounted for by the change in volume alone. The anomalies of water become easily explicable on some such basis, but will be more conveniently discussed when its behaviour. under pressure is considered.

This is the substance of McLeod's own summary. The temperature intervals used for calculating the two constants x_0 and A are not stated. In.a later paper [11] McLeod has recalculated x_0 from the viscosities at 0° and 10°; these figures are given in Table VIII, p. 105. The values of the free space found by using this small interval are considerably lower than those given in Table III—for hexane and heptane about 80 per cent., and for methyl alcohol about 56 per cent. only, of the latter. Some further difficulties arise when the values of the free space are compared with the compressibilities; this will be done in the next chapter, in which the relations between viscosity and pressure will be considered in detail. The calculation for the small interval from 0° to 10° was carried out with the object of reducing errors due to association, which should not change much within this small range; on the other hand, small errors in the viscosities produce large errors in x_0. The discrepancies between the values of the free space calculated from two different temperature intervals cannot, in any event, be due exclusively to association, since they are considerable even for unassociated liquids. While it must thus seem doubtful whether the free space calculated by McLeod's method is really the space not occupied by molecules, or possibly some simple function of it, it is evident that formula (9), when x_0 is determined for a suitable interval, represents the temperature function of viscosity better than the various interpolation formulæ given above. The defect of the method is that it represents viscosity as a function of volume only, whereas the data now available

on the variation of viscosity with pressure prove unambiguously that viscosity is not determined by volume alone.

Empirical Fluidity Formulæ. Empirical formulæ in which the fluidity ($\phi = 1/\eta$) appears have been put forward by Bingham.[12] They are

$$\phi = \frac{c}{\phi - at - b} \qquad . \qquad . \qquad . \qquad (10)$$

and

$$t = A\phi - B/\phi + C \qquad . \qquad . \qquad . \qquad (11)$$

The coefficients of the two equations are connected by the relations

$$A = 1/a, \quad B = c/a, \quad C = -b/a.$$

For water and other liquids containing hydroxyl groups these expressions prove inadequate, and a formula with four constants has to be employed:

$$t = A\phi + \frac{B}{\phi + D} + C \qquad . \qquad . \qquad . \qquad (12)$$

Another equation with four constants has also been suggested by Bingham:[13]

$$T = \alpha\phi - \beta + \gamma/\phi - \delta/\phi^2 \qquad . \qquad . \qquad (13)$$

This formula, in which T is the absolute temperature, represents Thorpe and Rodger's results for water and octane with a maximum deviation of 0.29 per cent., but is less accurate than Bingham's four-constant equation (12). In view of the comparatively simple character of the ϕ-t curves of most liquids, it is not surprising that they can be represented by equations with four constants, but the formulæ just given hardly show that the connection between fluidity and temperature is simpler, or more intelligible physically, than that between viscosity and temperature.

Porter's Relation between Temperatures of Equal Viscosity. The η-t curves of members of a homologous series show certain regularities, which will be more conveniently discussed in the chapter dealing with the connection between chemical constitution and viscosity. A very curious relation between the viscosities of pairs of—chemically quite unrelated—

liquids at different temperatures, discovered by Porter,[14] may, however, be mentioned here. When two liquids are examined through a sufficient range of temperature, a number of temperatures can generally be found for the second liquid, at which its viscosity is the same as that of the first liquid at a number of other temperatures. Let these temperatures, when those of the standard (first) liquid are T_0, be represented by T, then, if T/T_0 is plotted against T, the resulting curve is found to be practically a straight line. Fig. 26 (p. 64) shows this graph for mercury and water. The values used are as follows:—

η (Cp.).	T_0 (Water).	T (Mercury).	T/T_0.
1·6278	273 + 2°	273 + 4°	1·007
1·3077	10	78	1·346
1·0050	20	204	1·641
0·9142	24	340	2·063

(These values have been indicated by crosses on the η-t curves of water and mercury, fig. 26, p. 64.)

Porter points out that the method of plotting adopted is similar to that used by Ramsay and Young for comparing vapour pressures, for which he has shown that, if the T/T_0 curve is straight, then the vapour pressure of either liquid is given by

$$F(p) = A + B/T,$$

where F is the same function for both liquids. By analogy,

$$F(\eta) = A + B/T.$$

A formula of this type is stated to fit even so extreme a case as that of pitch, but Porter does not specify the function F for it.

Porter has examined other pairs of liquids, such as bromine and water, oil of turpentine and water, ethyl ether and benzene, and ethyl acetate and benzene; the results in all cases are the same as that for water and mercury. He points out the special interest attaching to this pair, because water is a strongly associated liquid, while mercury is considered non-associated. In the corresponding vapour-pressure problem a

deviation from straightness is generally held to indicate that " one of the vapours undergoes dissociation on heating," or that "there is molecular association in the liquid state." Since the T/T_0 line for water-mercury is straight, it would appear that the degree of curvature cannot be taken as evidence of association when viscosities are considered.

Batschinski's Formula. An interesting relation between the viscosity and the specific volume, put forward by Batschinski[15] and supported by a good deal of evidence, may be discussed here, since the specific volume is a function of temperature. This remarkably simple relation is

$$\eta = \frac{c}{v-\omega}, \qquad \frac{1}{\eta} = \frac{v-\omega}{c} . \qquad . \qquad . \qquad (14)$$

If, therefore, the specific volume v is plotted as ordinate against the fluidity, $1/\eta$, as abscissa, a straight line results. Batschinski has tested the formula on all the liquids investigated by Thorpe and Rodger, and obtained straight lines for practically all normal, *i.e.* unassociated, liquids. For associated liquids the lines show slight curvature, which is uniformly concave to the fluidity axis. Benzene gives a slightly curved graph of the same type, although it is not associated; Batschinski ascribes this to the fact that the temperature range, over which viscosity measurements extend, is very much nearer the freezing-point ($+5\cdot85°$) of benzene than it is for liquids which give perfectly straight graphs, like ethyl ether (freezing-point $-117\cdot6°$) and ethyl acetate (freezing-point $-82\cdot8°$). If a high freezing-point causes the curvature, it should be exhibited also by acetic acid, which Batschinski mentions as behaving anomalously, inasmuch as the graph is straight, although this liquid is also associated.

As regards the physical meaning of the constant ω, it may be defined as that specific volume of the substance, at which the viscosity becomes infinite. ω is therefore the " limiting volume " and $v-\omega$ the " free volume."

Batschinski has determined the constants c and ω for sixty-six liquids investigated by Thorpe and Rodger, and finds good agreement—maximum error about 1 per cent.—between the observed and calculated viscosity values. By

comparing ω with the critical volume, as determined by Young for nineteen of the liquids, he finds that the ratio ω/v_c deviates but slightly from a mean value 0·307, so that ω is approximately the parameter b of van der Waals's equation.

Discrepancies of Values for Free Space. If $(v - \omega)$ is the free space, equation (14) states that the viscosity is inversely proportional to it. This, as has been shown above, is McLeod's assumption, provided the exponent A = 1. It is of interest to compare the free spaces, say at 0°, calculated by the two authors. McLeod gives the free space in unit volume, while Batschinski, for a number of liquids, assumes the specific volume at 0° = 1 and calculates ω on this basis, so that $(1 - \omega)$ is the free space in unit volume at 0°, and should be the same as McLeod's x_0. A few of McLeod's and Batschinski's data are compared in Table IV.

TABLE IV

x_0 McLeod's free space at 0° calculated from large interval.
x_0' McLeod's free space at 0° calculated from interval 0° to 10°.
ω at 0° from Batschinski's tables.
$1 - \omega$ Batschinski's free space at 0°.

Substance.	x_0.	ω.	$1 - \omega$.	x_0'.
Hexane	0·1240	0·8897	0·1103	0·0979
Heptane	0·1052	0·9126	0·0874	0·0863
Octane	0·0940	0·9364	0·0636	0·0744
Ethyl iodide	0·1153	0·9048	0·0952	0·0907
Propyl iodide	0·0880	0·9263	0·0737	0·0782
Ethyl acetate	0·0853	0·9091	0·0909	0·0820
Propyl acetate	0·0830	0·9325	0·0675	0·0700
Toluene	..	0·9512	0·0488	0·0642
Chloroform	..	0·8967	0·1033	0·0945
Ethyl bromide	..	0·8772	0·1228	0·1080
Bromine	..	0·9162	0·0838	0·0740

Both authors used the same data for viscosities and thermal expansions; McLeod calculates x_0 (and x_0') by approximation, while Batschinski finds ω from the graph obtained by plotting $1/\eta$ against v. The differences between McLeod's two values

are considerable, and both differ from Batschinski's free space $(1-\omega)$; on the other hand, while the exponent of the free space is always $=1$ in Batschinski's formula, McLeod finds A different from, and practically always greater than, 1 for all the liquids in Table III. The two acetates are of particular interest, as the ϕ-v graph for ethyl acetate is conspicuously straight (*cf.* above), while McLeod finds the exponent $A=0.9425$ for it and both x_0 and x_0' considerably smaller than $(1-\omega)$; for propyl acetate $A=1.124$, and the difference in the free space is in the opposite direction.

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CHAPTER VI

THE VARIATION OF VISCOSITY WITH PRESSURE

IT has been mentioned (p. 7) that Coulomb raised the question whether pressure affected the resistance of water to the motion of the oscillating disc used by him, and attempted to answer it by carrying out experiments both at atmospheric pressure and *in vacuo*; no difference in the decrement could be detected.

Early Work. Experiments at higher pressures were first carried out almost simultaneously by Röntgen,[1] and by Warburg and Sachs,[2] who used capillary viscometers enclosed in glass piezometers. Röntgen observed a decrease in the viscosity of water with increasing pressure, and this result was confirmed by Warburg and Sachs, who used pressures up to 150 kg./sq. cm., and, in addition to water, examined liquid carbon dioxide, ether, and benzene. The viscosity of these three liquids increased with pressure.

Warburg and Sachs found that their results could be represented by a linear formula

$$\eta_p = \eta_0(1 + \alpha p),$$

in which η_0 and η_p are respectively the viscosity coefficients at atmospheric pressure and the pressure p, and α is a constant. If s is the reduction of volume produced by the pressure p,

$$\eta_p = \eta_0(1 + \beta s),$$

and the constants α and β are connected by the relation

$$\alpha = \beta z,$$

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z being the coefficient of compressibility. Warburg and Sachs give the following values of these constants:—

	Ether.	Benzene.	Water.
$a \times 10^6$	730	930	−170
$z \times 10^6$	173	91	45
β	2·5	4·2	−3·8

A further investigation was carried out by Cohen,[3] who studied water and sodium chloride solution of four different concentrations at various temperatures up to 25° and at pressures up to 900 atmospheres. He confirmed the previous results for water, and found a decrease of viscosity with increasing pressure at all temperatures; at 15·4° and 900 atmospheres the viscosity was 0·973, that at atmospheric pressure and the same temperature being taken as 1.

The behaviour of sodium chloride solutions was found to vary with the concentration; in dilute solutions the viscosity, like that of water, decreased slightly with increasing pressure, while in saturated solution it increased from 1 at atmospheric pressure to 1·045 at 600 atmospheres.

Hauser [4] extended the temperature range and thereby discovered a very interesting peculiarity of water. With rising temperature the effect of pressure decreases, and at about 32° disappears altogether, so that at this temperature the viscosity remains unaltered by an increase of pressure from 1 to 400 atmospheres. Above this temperature increase in pressure causes an *increase* in viscosity. Hauser's figures for the percentage change in viscosity between 1 and 400 atmospheres at different temperatures are given below.

Temperature.	$100(\eta_{400} - \eta_1)/\eta_1$.
30·5°	−0·5
31·5	±0·0
32·9	±0·0
36·0	±0·0
40·3	+0·7
57·0	+1·6

The capillary method was once more used by Faust,[5] who determined the viscosity of alcohol, ether, and carbon di-

sulphide at various temperatures and at pressures up to 3000 atmospheres. The viscosity-pressure curves found at three temperatures for ether and carbon disulphide, and four for alcohol, are given in fig. 27. Up to about 1500 atmospheres the viscosity increases in almost linear ratio with the pressure, but more rapidly at higher pressures. $\partial\eta/\partial p$ at constant
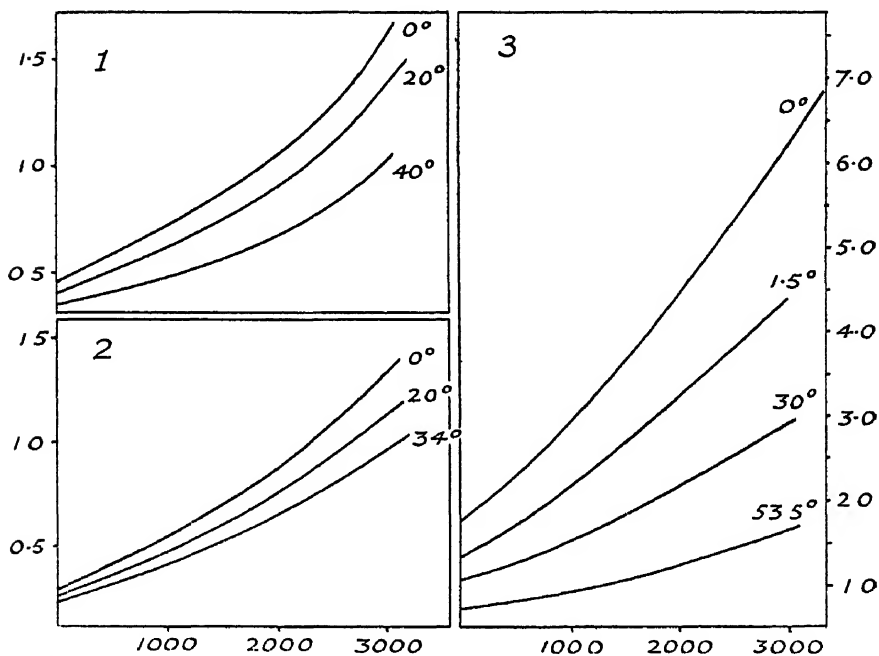
FIG. 27 —Viscosity-pressure curves (Faust) of (1) carbon disulphide, (2) ethyl ether ; (3) ethyl alcohol   Absc. kg./cm.², ord centipoises.

temperature is greatest for alcohol and smallest for carbon disulphide. The effect of pressure on the viscosity of ether varies little with rising temperature, the pressure at which η becomes double that at atmospheric pressure remaining practically constant. With alcohol, however, the temperature markedly reduces the pressure effect: while at 0° a pressure of 900 atmospheres doubles the viscosity, at 53·5° a pressure of 2200 atmospheres is required to produce this increase.

By drawing parallels to the axis of p in fig. 27, points are obtained on the curves representing equal values of η at different pairs of pressure and temperature. If the volumes

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(taken from Amagat's data) corresponding to these values of p and t are compared, they are found to be approximately constant for ether and carbon disulphide; for alcohol this simple relation does not hold, but the volumes at equal η decrease markedly with temperature. Faust points out that alcohol is highly associated, but concludes that for normal liquids the viscosity is an approximately linear function of the volume, and constant if the volume is kept constant. At constant pressure, in the region of high pressures, the viscosity is also an approximately linear function of the temperature, and the surface which represents the function (η, p, t) is a plane.

The Work of Bridgman. That these simple relations do not hold for an extended range of pressure and temperature,

FIG. 28.—Bridgman's apparatus for measuring viscosity at high pressures.

and that viscosity is certainly not merely a function of volume, is proved by the work of Bridgman.[6] His investigation far surpasses all previous ones in range and completeness, as he determined the viscosities of forty-three liquids at two temperatures, 30° and 75°, and at pressures up to 12,000 atmospheres.

The principle of Bridgman's method is as follows. A cylindrical hollow steel weight with hemispherical ends (fig. 28) falls in a steel tube of about 6 mm. internal diameter. The hollow weight is made in two pieces and can be loaded further with gold or tungsten weights; the annular space between it and the cylinder is from 0·0125 cm. (for water) to 0·075 cm. (for glycerin). Three small projections at a, a serve the double purpose of guiding the weight centrally and of making electric contact with the wall of the tube. The circuit is completed when the weight touches either of the electrodes e, e, which are insulated from the outer tube.

With an annular space of suitable width the time of fall

of the weight is proportional to the viscosity.   The tube can be rotated 180° while under pressure round a horizontal axis, thus causing the weight to fall; the current passing through the weight, which rests on the lower electrode, and the wall is interrupted, and is closed again when the weight has reached the other electrode.   This current through a suitable relay actuates an electric clock, which allows the time of fall to be measured with an error not exceeding $\frac{1}{120}$ second.   Two corrections are required: the weight begins to move before the cylinder has reached the vertical, and the weight moves some distance before it assumes a constant velocity.   A further correction must be applied to the buoyancy of the weight on account of the change in density of the liquid caused by the compression.   For details regarding these corrections, as well as the construction of the whole apparatus, the reader must be referred to the original.

For liquids which could be investigated up to 12,000 kg./cm.², readings were taken at 0, 100, 500, 1000, 2000, 4000, 6000, 8000, 10,000, and 12,000 kg./cm.² at 30°.   The temperature was then raised to 75° and the procedure reversed; if the boiling-point of the liquid lay above 75°, readings were continued down to atmospheric pressure; if below, the last reading was taken at a suitable pressure of a few kg./cm.²

To check the fundamental assumption that the times of fall are proportional to the viscosities, the times were determined for a number of liquids of known viscosities.   If the assumption is correct, the ratio of the times must be the same as the ratio of the corresponding viscosities, and this was found to be the case with satisfactory accuracy.   The whole investigation was of course directed to the determination of relative viscosities, the viscosity of any one liquid at atmospheric pressure and at 30° being taken as unity for all further determinations on the same liquid.

Table V gives the results for thirty liquids.   Water is again found to behave anomalously, and will be discussed below. The " General Character of the Results " is best described in the author's own words (p. 87).

TABLE V

VARIATION OF VISCOSITY WITH PRESSURE (BRIDGMAN)

Substance.	Pressure in kg./cm.²				
	1.	1000.	4000.	8000.	12,000.
Methyl alcohol, $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·769	0·167 $\bar{1}$·933	0·471 0·208	0·750 0·448	0·998 0·655
η_{30}/η_{75}	1·702	1·714	1·832	2·004	2·203
Ethyl alcohol . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·657	0·200 $\bar{1}$·873	0·617 0·289	1·023 0·634	1·390 0·919
η_{30}/η_{75}	2·203	2·123	2·128	2·449	2·958
n-Propyl alcohol $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·598	0·283 $\bar{1}$·880	0·836 0·368	1·402 0·827	1·915 1·223
η_{30}/η_{75}	2·523	2·529	2·938	3·758	4·920
n-Butyl alcohol $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·548	0·321 $\bar{1}$·867	0·934 0·312	1·609 0·941	2·208 1·396
η_{30}/η_{75}	2·845	2·858	3·343	4·679	6·518
n-Amyl alcohol $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·540	0·341 $\bar{1}$·871	1·060 0·466	1·811 1·049	2·495 1·562
η_{30}/η_{75}	2·884	2·951	3·926	5·781	8·570
i-Propyl alcohol $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·505	0·343 $\bar{1}$·851	0·982 0·425	1·640 0·957	2·311 1·424
η_{30}/η_{75}	3·141	3·120	3·624	4·844	7·748
i-Butyl alcohol $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·444	0·388 $\bar{1}$·824	1·203 0·488	2·075 1·158	2·898 1·747
η_{30}/η_{75}	3·597	3·664	5·188	8·260	14·16
i-Amyl alcohol $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·424	0·386 $\bar{1}$·787	1·185 0·492	2·069 1·168	2·952 1·780
η_{30}/η_{75}	3·805	4·012	4·970	8·042	15·76
n-Pentane $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·811	0·315 $\bar{1}$·163	0·847 0·676	1·360 1·119	1·846 1·493
η_{30}/η_{75}	1·545	1·419	1·483	1·742	2·254
n-Hexane $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·803	0·332 0·171	0·514 0·701	1·803 1·198	1·646
η_{30}/η_{75}	1·574	1·449	1·633	2·070	

TABLE V—*continued*

Substance.		1.	1000.	4000.	8000.	12,000.
n-Octane	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·810	0·327 0·153	1·088 0·763	 1·363	
	η_{30}/η_{75}	1·549	1·493	2·113		
i-Pentane	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·821	0·344 0·193	0·894 0·715	1·431 1·179	1·947 1·586
	η_{30}/η_{75}	1·510	1·416	1·510	1·786	2·296
Ethyl chloride.	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·850	0·242 0·131	0·649 0·514	1·008 0·834	1·323 1·111
	η_{30}/η_{75}	1·413	1·291	1·365	1·493	1·633
Ethyl iodide	$\log \frac{\eta_0}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·837	0·218 0·057	0·656 0·467	1·108 0·854	1·549 1·200
	η_{30}/η_{75}	1·455	1·445	1·545	1·795	2·234
Acetone	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·895	0·226 0·113	0·605 0·445	0·987 0·762	 1·031
	η_{30}/η_{75}	1·274	1·297	1·445	1·679	
Glycerin	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{2}$·810	0·260 $\bar{1}$·023	0·936 $\bar{1}$·529	1·741 0·094	 0·628
	η_{30}/η_{75}	15·49	17·26	25·53	44·36	
Carbon tetrachloride	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·760	0·351 0·100	 0·542		
	η_{30}/η_{75}	1·738	1·782			
Carbon disulphide	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·875	0·160 0·051	0·509 0·372	0·840 0·671	1·189 0·946
	η_{30}/η_{75}	1·334	1·285	1·371	1·476	1·750
Ethyl ether	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·878	0·324 0·149	0·792 0·601	1·261 0·986	1·670 1·311
	η_{30}/η_{75}	1·324	1·496	1·552	1·884	2·286
Chloroform	$\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$	0·000 $\bar{1}$·858	0·211 0·094	0·660 0·480	 0·914	
	η_{30}/η_{75}	1·387	1·309	1·514		

TABLE V—*continued*

Substance.		Pressure in kg./cm².·				
		1.	1000.	4000.	8000.	12,000.
Benzene . . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·765	0·347 0·081	 0·498 (3000)		
η_{30}/η_{75}		1·718	1·845			
Chloro-benzene . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·814	0·253 0·053	0·867 0·563	1·146	
η_{30}/η_{75}		1·535	1·585	2·014		
Bromo-benzene . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·801	0·262 0·044	0·897 0·558	1·029 (7000)	
η_{30}/η_{75}		1·581	1·652	2·183		
Aniline . . . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·551	0·376 $\bar{1}$·847	0·560		
η_{30}/η_{75}		2·812	3·381			
Toluene . . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·796	0·274 0·065	0·897 0·597	1·699 1·186	1·832
η_{30}/η_{75}		1·600	1·618	1·995	3·258	
o-Xylene . . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·767	0·311 0·057	0·689		
η_{30}/η_{75}		1·710	1·795			
m-Xylene . . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·799	0·290 0·079	0·967 0·637	1·333	
η_{30}/η_{75}		1·589	1·626	2·138		
p-Xylene . . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·797	 0·092			
η_{30}/η_{75}		1·596				
Eugenol . . $\log \frac{\eta}{\eta_0} \begin{cases} 30° \\ 75° \end{cases}$		0·000 $\bar{1}$·429	0·541 $\bar{1}$·810	2·273 0·805	2·343	
η_{30}/η_{75}		3·724	5·383	29·38		
Petroleum ether . $\log \frac{\eta}{r_0} \begin{cases} 30° \\ 75° \end{cases}$		0·00 ··	0·30 ··	0·93 0·56	1·59 1·06	2·18 1·49
η_{30}/η_{75}		··	··	2·34	3·39	4·90

" In certain qualitative features the behaviour of all the liquids investigated here, except water, is alike, although there are very large quantitative differences. The viscosity increases with pressure at a rapidly increasing rate, so that, if viscosity is plotted against pressure, a curve of very rapid upper curvature is obtained. This is unusual; most pressure effects become relatively less high at high pressure by a sort of law of diminishing return. In fig. 29 is shown viscosity against pressure at 30° for CS_2 and ether, two substances with comparatively small pressure effect. It is seen that over the first 2 or 3000 atmospheres the relation between viscosity and pressure is nearly linear, but above this the departure is extreme.
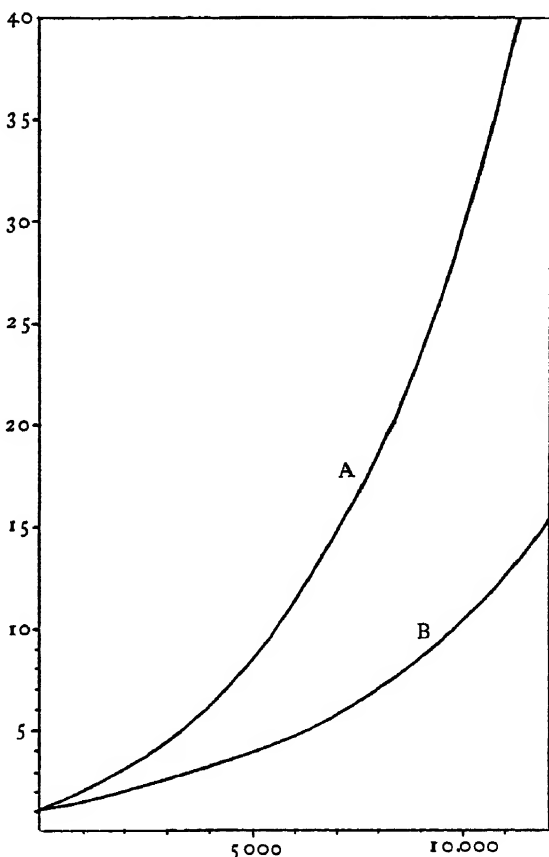
FIG. 29.—Relative viscosity-pressure curves (Bridgman) of (A) ethyl ether, (B) carbon disulphide. Ord η/η_0, absc. kg./cm.²

If log η is plotted against p a curve is obtained in general concave toward the pressure axis. The curvature is much the greatest at low pressure; above 2000 or 3000 kg. the curve approximates to a straight line, or indeed in a number of cases reverses curvature. This means that above 3000 kg. viscosity increases approximately geometrically as pressure increases arithmetically."

(Seventeen liquids show the opposite curvature.)

" The temperature coefficient of viscosity is shown by the rows in Table V, giving η_{30}/η_{75}. Here again the effect is abnormal; most temperature effects become less at high pressures, which is to be expected if the modification in the structure produced by temperature agitation becomes less under the greater constraints imposed by the high pressure. But here the relative change of viscosity with temperature becomes very markedly greater at high pressure, the ratio η_{30}/η_{75} changing under 12,000 kg. by a factor as much as 4.

" Apart from these qualitative resemblances, the most varied quantitative behaviour is shown by the various substances. In fact, viscosity is a unique property in regard to the magnitude of the pressure effect and its variation from substance to substance. The compressibility at atmospheric pressure, for example, varies by a factor of not more than 4- or 5-fold for the substances investigated here, and under 12,000 kg. the compressibility of any one substance diminishes by not over 15-fold. The thermal expansion changes by a factor of 2 or 3 under 12,000 kg. for these liquids, and the specific heats and thermal conductivities do not vary more. Excepting water, the smallest effect of pressure on viscosity found above is that on methyl alcohol, which increases 10-fold under 12,000 kg., and the largest is by over 10^7 for eugenol (obtained by linear extrapolation, which gives too low a value)."

Fig. 30 shows log η/η_0 plotted against the pressure for ether and carbon disulphide at 30°, and illustrates the rapid rise with increasing pressure. In fig. 33 (p. 95) the ordinates are the relative viscosities (η at 30° and atmospheric pressure $=1$) of carbon disulphide at 30° and 75°, while the abscissæ are the volumes, the volume at atmospheric pressure and 0° being taken as unity. It appears clearly from this graph that the *viscosities at equal volume are not equal*, so that viscosity is not a function of the volume alone, as suggested by Faust. This important point is discussed more fully on p. 95.

Anomaly of Water. The anomalous behaviour of water, found at comparatively low pressures by Hauser, is confirmed by Bridgman. " Water is quite different in character from

other liquids.   Previous investigations have been made by
Hauser up to 400 kg./sq. cm.   He found that, below 30°,
viscosity decreases with increasing pressure, and above 30°
increases.   At higher pressures we now find that at 0° and
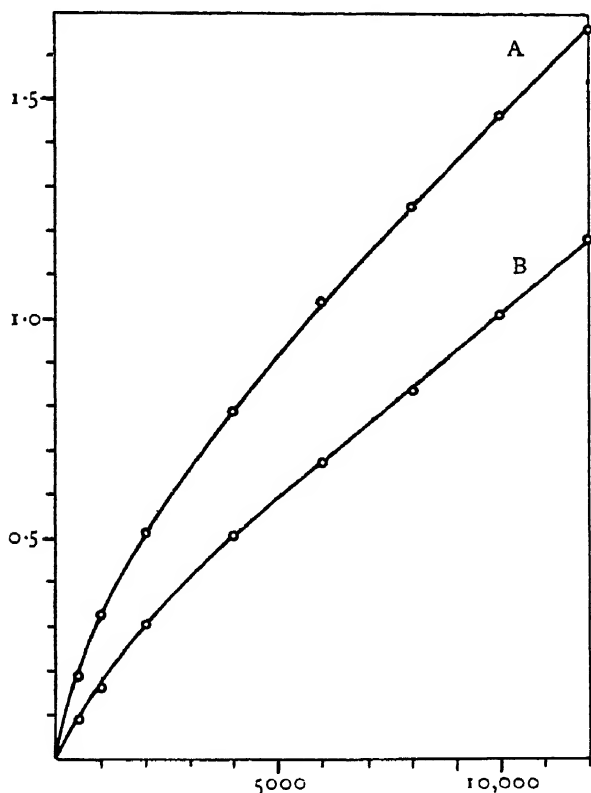
FIG 30.—Log (η/η_0)-pressure curves (Bridgman) of (A) ethyl
ether ; (B) carbon disulphide.

10° there is a minimum viscosity at a pressure of roughly
1000 kg., the minimum being less pronounced at 10° than
at 0°.   At 30° and 75° there is a regular increase of viscosity
with pressure over the entire range.   (Not much weight must
be placed on the precise numerical values given for 75°, there
being much experimental uncertainty here because of electrical
conductivity of the water.)   It is natural to see in this abnormal
behaviour of water an association effect; at low temperatures
and pressures water is strongly associated with large molecules

and a large viscosity, but as pressure increases the association decreases, and the average size of the molecules decreases, giving a term in the viscosity which diminishes fast enough to more than compensate the normal increase of viscosity under pressure. At higher pressures the association effect is exhausted, and the behaviour is normal."

Fig. 31 shows the viscosity of water at 0°, 10°, 30°, and·
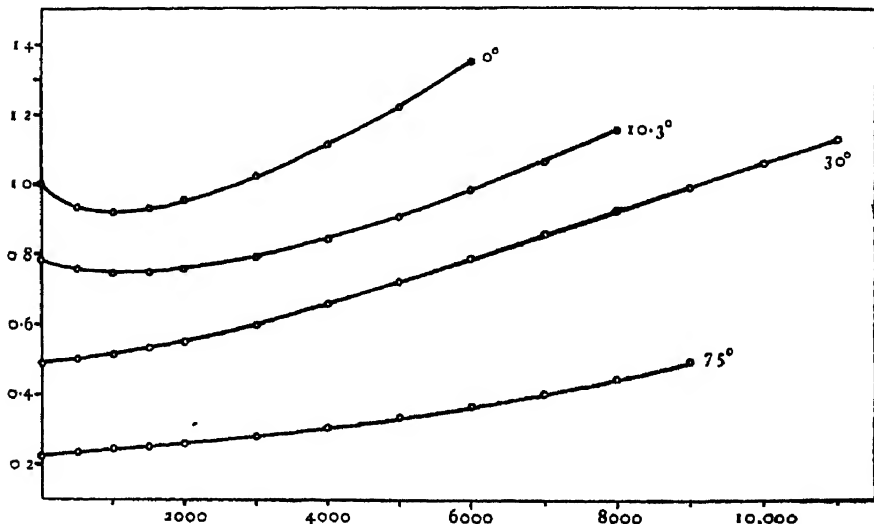
FIG. 31.—Relative viscosity-pressure curves of water at four temperatures (Bridgman).

75° plotted against the pressure, and illustrates the anomalous behaviour just described.

McLeod's and Batschinski's Formulæ applied to Bridgman's Data. As the data on the effect of pressure on viscosity were scanty before Bridgman's investigation, no attempt appears to have been made to discover empirical equations for it. Batschinski's formula (p. 76), however, contains the specific volume, and it is therefore possible to test it by applying it to Bridgman's data. It will be sufficient to determine one constant, c; if two pairs of values of v and η are given, we have:

$$c = \frac{(v_1 - v_2)\eta_1\eta_2}{\eta_2 - \eta_1}.$$

Bridgman's data for ethyl ether at 30° are:

$$v_1 \text{ (atmospheric pressure)} = 1 \cdot 0492, \quad \eta_1 = 1 \cdot 000.$$
$$v_2 \text{ (4000 kg./sq. cm.)} = 0 \cdot 8318, \quad \eta_2 = 6 \cdot 195.$$
$$v_3 \text{ (8000 kg./sq. cm.)} = 0 \cdot 7675, \quad \eta_3 = 18 \cdot 24.$$

Calculated from $v_1 \, \eta_1, \, v_2 \, \eta_2, \, c = 0 \cdot 2592.$
Calculated from $v_1 \, \eta_1, \, v_3 \, \eta_3, \, c = 0 \cdot 2980.$

So that the formula cannot be said to hold even approximately.

In the paper already quoted (p. 70) McLeod has also attempted to find an expression for the variation of viscosity with pressure in terms of free space; the only data then available, covering a fairly extensive range, were those of Faust. If the assumption is made that the whole decrease of volume under pressure takes place at the expense of the free space, the calculated values are much too low. It must therefore be assumed that a compression of the molecules themselves also occurs, and if this reduction is further assumed to be proportional to the pressure, a simple expression for the value of the free space at different pressures can be deduced. If C is the *total* contraction under pressure P, the contraction of the free space will be C−BP, where B is a constant for a given liquid. If x_0 is again the free space at 0° and atmospheric pressure, the free space at temperature t and pressure P will be

$$x_{Pt} = (x_0 + \alpha t + \beta t^2 + \gamma t^3) - (C - BP) \quad . \quad . \quad (1)$$

McLeod applies this formula to Faust's results for carbon disulphide at 0°, 20°, and 40°, and at pressures up to about 3000 kg./sq. cm., and finds good agreement. He gives the following constants for this liquid:—

$$\alpha = 0 \cdot 0_2 11398, \quad \beta = 0 \cdot 0_5 1137, \quad \gamma = 0 \cdot 0_7 1912,$$
$$x_0 = 0 \cdot 1300, \quad B = 0 \cdot 0_5 96.$$

The viscosity is calculated on the assumption (*cf.* p. 70) that the exponent A = 1, so that $\eta_0 x_0 = \eta_P x_P$.

It is of interest to apply McLeod's calculation to the much greater interval covered by Bridgman's work. The figures for

carbon disulphide at 30° are:

> Volume at atmospheric pressure $v_0 = 1\cdot0357$.
> Volume at 12,000 kg./sq. cm.　　$v_p = 0\cdot7658$.
> Total contraction　　　　　　　　C $= 0\cdot2699$.

This gives a value of $0\cdot0113$ for the free space at 30° and 12,000 kg. pressure, and a relative viscosity (η at 30° and atmospheric pressure $=1$) $\eta_P = 14\cdot69$, whereas the value found experimentally by Bridgman is $15\cdot40$. Considering that the constant B has been determined for the comparatively small interval to 3000 kg., the agreement is decidedly satisfactory.

McLeod states that a similar calculation for ether also represents Faust's results satisfactorily. He gives the following constants for this liquid:—

$$a = 0\cdot0_2115056, \quad \beta = 0\cdot0_51116, \quad \gamma = 0\cdot0_71745,$$
$$x_0 = 0\cdot1400, \quad B = 0\cdot0_4175.$$

Bridgman's data for ether at 30° are:

> Volume at atmospheric pressure $v_0 = 1\cdot0492$.
> Volume at 12,000 kg./sq. cm.　　$v_p = 0\cdot7237$.
> Total contraction　　　　　　　　C $= 0\cdot3255$.

This gives a value of $0\cdot0610$ for the free space at 30° and 12,000 kg., and a relative viscosity $\eta_P = 2\cdot894$, while the value of the latter given by Bridgman is $46\cdot78$. The method of calculation therefore fails completely. One reason for the failure may be a curious discrepancy in the figures for the contraction of the free space, $C - BP$, calculated from Bridgman's data for C and McLeod's value for B. These figures are:

Pressure (kg./sq. cm.) .	2000	4000	8000	12,000
C	0·1512	0·2174	0·2817	0·3255
C − BP . . .	0·1162	0·1474	0·1417	0·1155

The contraction of the free space passes through a maximum at about 4000 kg. pressure and then decreases. Obviously this is not possible, but the contraction of the free space must increase continuously—as, indeed, it does with carbon disulphide. It is equally obvious that this discrepancy cannot

be due merely to the constant B having been determined from too small an interval, but indicates some defect in the method. The equation (1) for the free space at temperature t and pressure P contains the assumption that a portion of the contraction at *all* pressures, however low, is due to compression of the molecules—an assumption which may be correct, but hardly seems as plausible as the alternative, that compression of the molecules does not begin until a certain reduction of the free space has taken place. The P-V
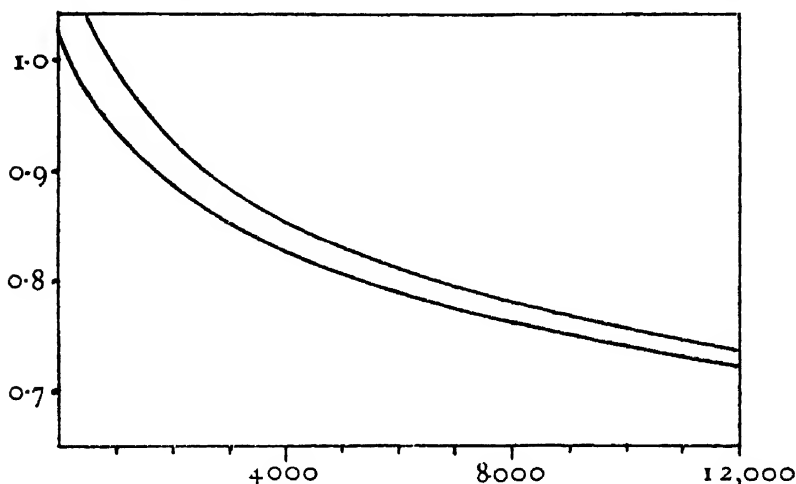
FIG. 32 —Volume-pressure curves of ethyl ether at 30° and 70° (Bridgman).   Volume at 0° and 1 kg./cm.² = 1.

curves give no definite information on this point, as they exhibit no abrupt change of curvature, although in all of them dv/dp decreases markedly with increasing pressure.   A typical curve, that for ether, is shown in fig. 32.

In view of the failure of formulæ assuming a simple relation between viscosity and free space, it is perhaps of interest to compare the values of the latter, as calculated by McLeod, with the volumes at different pressures determined by Bridgman.   Table VI gives in the first column McLeod's free space at 0° and atmospheric pressure, while the remaining columns give Bridgman's data for the volume occupied by the liquids at 20° and at different pressures; the volume at 0° and atmospheric pressure is taken as unity.

TABLE VI

FREE SPACE AT 0° (x_0) COMPARED WITH REDUCTION OF VOLUME BY PRESSURE (M^{c}LEOD and BRIDGMAN)

Substance.	x_0.	Volume at pressure of	
		4000 kg./cm.²	12,000 kg./cm.²
Ethyl iodide . . .	0·1153	0·8583	0·7588
Dimethyl ketone . .	0·1430	0·8532	
Methyl alcohol . .	0·1037	0·8551	0·7559
Ethyl alcohol . .	0·09215	0·8545	0·7521
Propyl alcohol . .	0·0333	0·8700	0·7840
Iso-butyl alcohol . .	0·0645	0·8601	0·7662
Mercury (22°) . .	0·0443	0·9809	0·96596

Examination of these figures reveals some very striking discrepancies. Apart from mercury, the reduction in volume at 4000 kg./cm.² is about 14 per cent. for all the liquids (13 per cent. for propyl alcohol), and already exceeds the free space, which varies from 14·3 per cent. (dimethyl ketone) to 3·3 per cent. (propyl alcohol). At 12,000 kg./cm.² the volume of all the liquids is reduced by about 24 per cent. (22 per cent. for propyl alcohol), so that the excess over the free space of about 10 per cent. of the volume at 0° and atmospheric pressure represents actual compression of the molecules.

Even more striking are the figures for propyl alcohol, especially when compared with those for mercury. The free space of propyl alcohol, 3·33 per cent., is only a little over one-third of that of the next lower homologue, ethyl alcohol, and actually lower than that of mercury, 4·43 per cent. Yet the compressibility of propyl alcohol is very little smaller than that of the other alcohols: the reduction in volume at 12,000 kg./cm.² amounts to 21·6 per cent., so that the reduction in the space occupied by the molecules themselves amounts to 18·27 per cent., or about 5·5 times the free space. On the other hand, while the free space of mercury (calculated from ρ and η at 0° and 100°) at 0° is 4·43 per cent., the reduction in volume at 12,000 kg./cm.² amounts to only 3·41 per cent., so that there is nearly a quarter of the free space still left.

The question how far compressibility can be ascribed to reduction of free space has been discussed by Bridgman: "All ordinary liquids show a decreasing compressibility with rising pressure, the compressibility decreasing faster than the volume, and they also show an increasing compressibility with rising temperature. The mathematical equivalent of this last statement is that the thermal dilatation decreases with increasing pressure. This normal behaviour is exactly as we would expect if we regard the liquid as composed of nuclei of more or less variable volume, separated by space which may be altered by pressure and temperature." . . . "It is to be noticed that in assuming that the molecules are compressible we have not by any means assumed that the actual change of size of the molecules under pressure is the chief factor in the change of volume of the substance as a whole under pressure. In fact it is almost certainly true that the greater part of the total change of volume is due to the closing of the space between the molecules."

Fig. 33.—Viscosity-volume curve of carbon disulphide at 30° and 75° (Bridgman). Absc volume, ord. $\eta / _{,0}$

Since Batschinski's and McLeod's are the only attempts to establish a rational connection between viscosity and volume, it seems justifiable to call attention to these difficulties, although Bridgman's results show quite conclusively that viscosity, at any rate at high pressures, cannot be merely a function of the volume. In fig. 33 the viscosity of carbon disulphide at 30° and 75° is plotted against the volume: at

equal volume it is always lower at the higher temperature. Fig. 34, in which the ordinates are the common logarithms of the viscosity of amyl alcohol, and the abscissæ again volumes, shows the effect of temperature at equal volume even more strikingly. The assumption that viscosity decreases with rising temperature merely because the volume— or the free space—increases is therefore not tenable, although at atmospheric pressure the greater part of the temperature effect may quite probably be due to the thermal expansion. Bridgman emphasises this conclusion: "The few theoretical discussions of liquid viscosity have all attached especial significance to the relation between viscosity and volume. Faust drew from his measurements the conclusion that at high pressures viscosity tends to a limiting behaviour, in which it is a linear function of volume only, so that the viscosity is constant at a given volume independent of temperature (pressure varying). This be-

FIG. 34.—Log (η/η_0)-volume curves of amyl alcohol at 30° and 75° (Bridgman).

haviour he found for carbon disulphide and ether in the pressure range of 3000 kg., but he found that ethyl alcohol did not approach such a behaviour. The new data of this paper show that at high pressures the viscosity of all substances departs very far indeed from being a linear function of volume at a definite temperature, or from being a pure volume function of any kind." The principal problem which any theory of the viscosity of liquids will have to solve is to explain this effect of temperature at constant volume. Various attempts at such theories have been shown by Bridgman to lead to numerical results quite irreconcilable with his experimental data.

A theory which accounts qualitatively for the decrease in viscosity with rising temperature at constant volume has quite recently been put forward by Andrade;[7] its discussion is beyond the scope of this work.

Effect of Pressure and Molecular Structure.   The great differences between the magnitudes of the pressure effect in different liquids have already been discussed.   Bridgman draws the following conclusions from his results: "In general, the largest pressure effects are for those substances with the most complicated molecules.   This is very plainly shown by the series of alcohols, or by the various compounds derived from benzene; the relative pressure effect is greater the more complicated the group substituted for hydrogen.   There is also a very marked constitutive effect, the iso-compounds having a larger effect than the normal compounds, and a similar effect is seen in the three xylenes.   A heavier atom substituted into a molecule produces in general a larger pressure effect, as is shown in the series ethyl chloride, bromide, and iodide, or by chloro- and bromo-benzene."

[1] W. C. Röntgen, *Wied. Ann.*, **22**, 510 (1884).
[2] E. Warburg and J Sachs, *ibid.*, **22**, 518 (1884).
[3] R. Cohen, *ibid* , **45**, 666 (1892).
[4] L. Hauser, *Drude's Ann.*, **5**, 597 (1901).
[5] O Faust, *Zeit physik Chem* , **86**, 479 (1914)
[6] P W Bridgman, *Proc Nat. Acad Amer* , **11**, 603 (1925) •
[7] E. N da C Andrade, *Engineering*, **124**, 462 (1927). .

CHAPTER VII

VISCOSITY AND CONSTITUTION

Thomas Graham in a paper published in 1863 makes the following remark: " Perhaps the most interesting part of the further development of the subject here discussed may prove to be the investigation of the transpiration of homologous substances." [1] He himself had already measured the transpiration times of several alcohols, ethers, and fatty acids, and suggested that there might be a regular increase as a homologous series was ascended, parallel with the rise in boiling-point recently found by Kopp.

The first extensive investigation undertaken with the object of comparing the viscosities of members of homologous series was carried out by Rellstab. [2] The author has not had access to this publication, which is, however, extensively quoted by Přibram and Handl (*vide infra*). Rellstab considered the proper basis of comparison to be, not the transpiration times of equal volume, but of equivalent weights, *i.e.* of volumes containing the same number of molecules. He also recognised the necessity of comparing the transpiration times at corresponding temperatures, and assumed that temperatures of equal vapour pressure were such; the vapour pressure data were taken from measurements carried out about the same time by Landolt. His results, which have been confirmed qualitatively by later investigators, amount to the following: the transpiration time decreases for all liquids with rising temperatures; it increases with each increment of CH_2 in every homologous series, and it is different for metamers.

Guerout [3] seven years later investigated a number of organic liquids by Poiseuille's method; the brief account published

gives no details of the apparatus used.   He finds that the transpiration times increase as the series of alcohols is ascended, but do not do so regularly.   He comments on the great increase between methyl and ethyl alcohol, and also on the absence of any parallelism between transpiration time and density.

In a series of three papers Přibram and Handl [4] give the results of measurements on a very large number of organic compounds, expressed as transpiration times for equal volumes, equivalent weights, and also as relative viscosities.   They confirm much of Rellstab's work: apart from the first members, the increase in viscosity in successive members of a homologous series is roughly proportional to the increment in CH_2; substitution of halogen or NO_2 for hydrogen increases the viscosity (though they incline to the opinion that the effect of NO_2 is more profound than mere substitution); they also, for the first time, point out that normal esters are more viscous than the iso-compounds, and that this holds whether the normal radical is the alcohol or the acid radical; and finally that the alcohols have higher viscosities than the corresponding ketones.

Gartenmeister [5] determined the absolute viscosity of no less than twelve hydrocarbons and their chlorine substitution products, ten alcohols, fifteen acids, sixteen ethers, twelve ketones, and sixty-three esters, all carefully purified.   From these data he deduces the following relations between the molecular weight M and the viscosity coefficient:—

(1) η/M =const. within the limits of experimental error for compounds with the same number of carbons, and with some exceptions at all temperatures.   This holds, *e.g.*, for propyl and allyl chloride, bromide, and iodide respectively.

(2) η/M^2 =const. at all temperatures for all series in which successive members differ by CH_2.

Gartenmeister emphasises that η/M^2 is " not a constant in the sense of the mathematician, but a physico-chemical constant," the variation of which may be sufficiently illustrated by one example:

	Pentane.	Hexane.	Heptane.	Octane.	(All at 0°.)
$(\eta \times 10^7)/M^2=$	54·5	53·6	51·9	54·1	

He also calls attention to the great increase in viscosity produced by OH, and gives as example n-propyl alcohol, propylene-glycol, and glycerol:

	$C_3H_7OH.$	$C_3H_6(OH)_2.$	$C_3H_5(OH)_3.$
$(\eta \times 10^7)/M^2 =$	63	79	100

Thorpe and Rodger's Work. Neither Přibram and Handl nor Gartenmeister attempted to find " molecular " and " atomic " viscosity values, *i.e.* figures by the addition of which the viscosity of compounds could be found; indeed, they express considerable doubts whether such a course is possible. This attempt was made for the first time by Thorpe and Rodger,[6] whose apparatus has already been described (p. 40), while the viscosities of a number of—very carefully purified— liquids investigated by them have been given in Table I, pp. 66–67. The viscosity-temperature curves found experimentally were all plotted on a large scale, and the authors clearly realised the fundamental difficulty in the way of comparing the viscosities in any homologous series, viz. the rational choice of a temperature of comparison. Thorpe and Rodger compared viscosities at the boiling-point and at temperatures " of equal slope," *i.e.* temperatures at which $d\eta/dt$ had the same value. If these temperatures are compared for successive members of homologous series, it is found that they increase fairly regularly for each increment of CH_2. They further found that if the viscosities are η_1 and η_2 at two temperatures t_1 and t_2 corresponding to two arbitrarily chosen values of $d\eta/dt$, the ratio η_1/η_2 is approximately constant ($=2\cdot03$) for thirty-three liquids, when the temperatures are those corresponding to $d\eta/dt=0\cdot0_4987$ and $0\cdot0_4323$. This suggested to them that the temperatures of equal $d\eta/dt$ are corresponding temperatures in respect of viscosity.

Comparison at temperatures of equal slope confirms generally the earlier results: the viscosity in homologous series increases with each increment of CH_2, but the increase becomes smaller with increasing molecular weight. The alcohols and acids behave anomalously. Iso-compounds have lower viscosities than the corresponding normal compounds. Associated liquids have much higher temperature coefficients

of viscosity than non-associated, and the first two or three in a series exhibit anomalies, as they do in respect of other physical properties. The anomaly is most pronounced in the fatty acid series, formic and acetic acids being more viscous than propionic at all temperatures up to 100°.

Thorpe and Rodger endeavoured to get more definite quantitative relations by introducing functions of the molecular volume. If this is V, $V^{2/3}$ is the " molecular surface " and the product $\eta V^{2/3}$, *i.e.* the force required per molecular surface to maintain unit velocity gradient they described as " molecular viscosity." $V^{1/3}$ is a length containing equal numbers of molecules for different substances, and the product $\eta V^{2/3} \times V^{1/3} = \eta V$ is the work required to move a " molecular surface " through a " molecular length " while maintaining unit velocity gradient. This quantity Thorpe and Rodger called the " molecular viscosity work."

It is not very easy to find any physical meaning in the various quantities just defined, or to look on them as anything but somewhat arbitrary functions of the molecular volume, which lead to more regular empirical relations than do the viscosities alone. Such can be found, as we shall see, by using even more arbitrary functions, like the logarithm of the molecular weight.

The comparison of molecular viscosities at the boiling-point leads to results which are in general parallel to those found by comparing the absolute viscosities at these temperatures, but additive relations become somewhat clearer. They are still more so when molecular viscosities are compared at temperatures of equal slope, *i.e.* equal $d\eta/dt$. The increment for each CH_2 becomes more regular, and, although the first members of each series still show anomalies, the increment of molecular viscosity does not deviate much from a mean value of 120 ($\eta \times V^{2/3} \times 10^4$).

Fluidity and Association. Bingham[7] takes the view that fluidities provide a better basis of comparison than viscosities, because the temperature-fluidity function is nearly linear, especially at high temperatures. The ϕ-t lines of substances belonging to homologous series are parallel, and the fluidities at the boiling-points are very nearly equal when the liquids are not

associated. The ϕ-t graphs are markedly curved for alcohols, ketones, and acids, while the fluidities at the boiling-points show considerable differences. Such deviations from linearity Bingham ascribes to association, and points out that the ϕ-t graph of mercury, which is probably the nearest approach to a liquid consisting of single molecules, is almost exactly straight, and intersects the temperature axis about the absolute zero, *i.e.* $\phi = 0$, or $\eta = \infty$ at this point. This is quite true for temperatures below about 130°, but above these the ϕ-t curve (plotted from Koch's data for the viscosity of mercury) becomes markedly curved and concave to the temperature axis; nor is it quite easy to see what the fluidity at temperatures below the freezing-point can mean.

At all events, the approximately linear character and the parallelism of the curves for a given series makes comparison easier, as $d\phi/dt$ is characteristic of the series, and the distance on the t-axis between successive curves is a measure of the effect of a CH_2 group.

Bingham finds that, when liquids are compared at temperatures of equal fluidity, the temperature increment for a CH_2 and for various other groups and atoms is regular, and, moreover, has the same value for different series, whereas the increments found by Thorpe and Rodger differed from series to series. Temperatures of equal fluidity are also, very approximately, temperatures of equal vapour pressure, and thus represent corresponding conditions.

Bingham and Harrison [8] have carried out the calculation of the temperature increments at the fluidity $=200$ ($1/\eta$ poises) for various groups and atoms, and find the fluidity so nearly additive that the temperature corresponding to $\phi = 200$ can be found as the sum of the values for the groups and atoms constituting a given compound, provided it is not associated. For associated liquids the temperatures calculated from constants derived from non-associated liquids are always considerably lower than the temperature actually observed, and in view of the additive character of these constants, Bingham considers that the degree of association can be found by simply dividing the observed by the calculated temperature.

Table VII gives a number of observed and calculated values

of the temperatures corresponding to $\phi=300$, and the degree of association calculated from them as just described; the fourth column gives the degree of association for $\phi=200$, that is, at lower temperatures. When the degree of association changes in the intervals contemplated, it is, as one would expect, higher at $\phi=200$, viz. at lower temperature.

TABLE VII

ASSOCIATION FACTORS AT FLUIDITIES $\varphi=200$ AND 300
(BINGHAM)

Substance.	$\varphi=300.$		$\varphi=300.$	$\varphi=200.$
	Temp. obs.	Temp. calc.	Assoc. factor.	Assoc. factor.
Water	358·5	162·7	2·20	2·31
Dimethyl ketone . .	289·5	207·5	1·23	1·23
Diethyl ketone . .	326·5	285·4	1·14	1·14
Methyl ethyl ketone . .	315·6	260·0	1·21	1·22
Methyl propyl ketone . .	330·0	285·4	1·17	1·16
Acetic acid . . .	407·9	236·3	1·73	1·77
Propionic acid . .	408·5	261·7	1·55	1·57
Butyric acid . .	413·7	287·1	1·48	1·51
Iso-butyric acid . .	413·7	278·9	1·49	1·51
Acetic anhydride . .	388·1	309·9	1·25	1·25
Benzene . . .	348·1	303·7	1·14	1·17
Toluene . . .	347·5	329·1	1·06	1·06
Ethyl benzene . .	362·1	354·5	1·02	1·02
o-Xylene . . .	377·5	354·5	1·06	1·07
p-Xylene . . .	357·4	354·5	1·00	1·00
Methyl alcohol . .	336·9	188·1	1·79	1·84
Ethyl alcohol . .	(371·5)	213·5	(1·74)	1·83
Active amyl alcohol .	(408·7)	289·7	(1·41)	1·54
Inactive amyl alcohol .	(415·5)	289·7	(1·30)	1·55
Allyl alcohol . . .	378·7	234·6	1·61	1·69
Methyl formate . .	297·5	236·3	1·26	(1·25)
Ethyl formate . .	311·4	261·7	1·19	1·19
Propyl formate . .	333·9	287·1	1·16	1·17
Methyl acetate . .	306·0	261·7	1·17	1·17
Ethyl acetate . .	320·8	287·1	1·12	1·17
Propyl acetate . .	343·0	312·5	1·09	1·12

Since this method of calculating association factors involves rather considerable assumptions, it is of interest to compare the values thus found with those given by other observers

using different methods. This will be done below, when McLeod's treatment of the problem has been discussed.

McLeod's Theory. His paper,[9] of which the following is a summary, begins by recalculating (as has been briefly mentioned on p. 73) the values of the free space at 0° from data for the small interval from 0° to 10°, the object being to eliminate as much as possible the effect of any change in the degree of association. If v_{10} is the volume occupied at 10° by the mass of liquid occupying 1 c.c. at 0°, the free space per c.c. at 10° will be $(x_0 + v_{10} - 1)/v_{10}$, and assuming the exponent A to be $= 1$ (*cf.* p. 70),

$$\frac{\eta_0}{\eta_{10}} = \frac{x_0 + v_{10} - 1}{x_0 v_{10}}.$$

Table VIII gives, in column 4, the values of x_0 thus calculated, while column 5 shows those of v_{10}. Column 1 gives the observed values of η at 0°, and column 2 η for each liquid " with the free space adjusted to a fixed ratio to the total volume, viz. 0·100." These values of η are calculated on the same assumption, that the viscosity varies inversely as the free space, and if this were strictly correct, the method would amount to comparing viscosities at temperatures of equal free space.

McLeod then plots these viscosities at free space $= 0·1$ against the molecular weights (in the gaseous phase); a few typical points only are shown in fig. 35. They appear at first sight to be distributed quite irregularly, but it can be observed that the points for substances generally considered as non-associated fall approximately on a straight line passing through the origin. Associated liquids have viscosities too high in proportion to their molecular weight to fall near this line—in other words, the molecular weight would have to be increased to bring them on it.

McLeod assumes as the normal line, $\eta = k\mathrm{M}$, in the viscosity-molecular weight diagram that which passes through the point for octane, the degree of association of which is given by Ramsay and Shields [10] as $= 0·93$. McLeod then calculates the factor a, by which the molecular weight has to be multiplied to bring the points η-$a\mathrm{M}$ on the octane line.

TABLE VIII

Viscosities Corrected for Free Space = 0·100 and Association Factors (McLeod)

| Substance.	η_0.	η_0 corr. for free space 0·100.	M.	x_0.	v_{10}.	Assoc. factor.
Pentane	0·283	0·342	72·1	0·1207	1·01497	0·96
Hexane	0·3965	0·388	86·1	0·0979	1·01285	0·92
Iso-hexane	0·371	0·391	86·1	0·1054	1·01383	0·92
Heptane	0·519	0·448	100·1	0·0863	1·01223	0·91
Octane	0·703	0·523	114·1	0·0744	1·01203	0·93
Ethyl iodide	0·719	0·653	156·0	0·0907	1·01155	0·85
Propyl iodide	0·938	0·735	170·0	0·0782	1·01146	0·88
Iso-propyl iodide	0·8785	0·735	170·0	0·0836	1·01230	0·88
Acetone	0·394	0·447	58·0	0·1134	1·01383	1·56
Methyl ethyl ketone	0·5385	0·445	72·0	0·0827	1·01220	1·25
Formic acid	2·245	0·800	46·0	0·0356	1·00968	3·53
Acetic acid	1·219	0·687	60·0	0·0564	1·01061	2·38
Propionic acid	1·519	0·855	74·0	0·0563	1·01094	2·35
Butyric acid	2·284	0·953	88·0	0·0417	1·01034	2·20
Iso-butyric acid	1·885	0·874	88·0	0·0463	1·01000	2·00
Methyl alcohol	0·813	0·471	32·0	0·0580	1·01148	2·99
Ethyl alcohol	1·770	0·795	46·0	0·0450	1·01051	3·50
Propyl alcohol	3·882	0·902	60·0	0·0233	1·00797	3·95
Butyl alcohol	5·185	1·286	74·0	0·0248	1·00866	3·53
Iso-propyl alcohol	4·564	1·150	60·0	0·0252	1·01061	3·89
Iso-butyl alcohol	8·038	1·950	74·0	0·0243	1·01145	5·25
Ethyl acetate	0·578	0·474	88·0	0·0820	1·01263	1·09
Propyl acetate	0·770	0·539	102·0	0·0700	1·01197	1·07
Ethyl ether	0·286	0·353	74·1	0·1234	1·01518	0·97
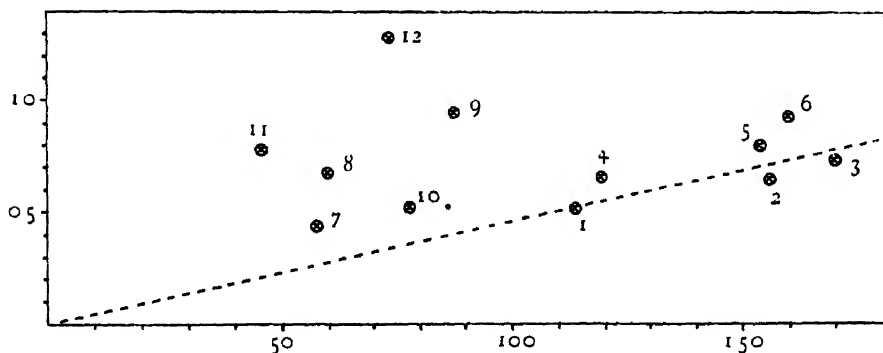
FIG. 35 —McLeod's graph illustrating association 1, octane; 2, ethyl iodide; 3, propyl iodide, 4, chloroform, 5, carbon tetrachloride; 6, bromine; 7, acetone; 8, acetic acid; 9, butyric acid; 10, carbon disulphide; 11, ethyl alcohol; 12, butyl alcohol.

In Table IX the values thus calculated are shown in the first column, while the others give association factors found by different methods by (2) Ramsay and Shields (*loc. cit.*), (3) Bingham by the method described above, and (4) Traube.[11]

TABLE IX

VALUES OF ASSOCIATION FACTORS BY VARIOUS METHODS

Substance.	McL.	R. and S.	B.	T.
Octane	0·93	0·93		
Ethyl iodide	0·85	1·01		
Ethylene bromide . . .	1·21	..	1·09	
Bromine	1·18	..	1·15	
Ethylene chloride . . .	1·42	..	1·21	1·46
Carbon tetrachloride . .	1·05	1·01		
Carbon disulphide . . .	1·39	1·07		
Acetone	1·56	1·26	1·23	1·53
Methyl propyl ketone . .	1·13	1·11	1·17	1·43
Formic acid	3·53	3·61	..	1·80
Propionic acid . . .	2·35	1·77	1·55	1·46
Butyric acid	2·20	1·58	1·48	
Iso-butyric acid . . .	2·00	1·45		
Acetic anhydride . . .	1·34	0·99	1·25	
Propionic anhydride . .	1·22	..	1·11	
Ethyl ether	0·97	0·99		
Benzene	1·37	1·01	1·14	1·05
Toluene	1·08	..	1·06	
Ethyl benzene . . .	0·91	..	1·02	
o-Xylene	1·02	..	1·06	
m-Xylene	0·92	..	1·00	
Methyl alcohol . . .	2·99	3·43	1·79	1·79
Ethyl alcohol. . . .	3·50	2·74	1·74	1·67
Propyl alcohol . . .	3·05	2·25	..	1·66
Butyl alcohol. . . .	3·53	1·94		
Allyl alcohol	2·77	..	1·61	
Iso-propyl alcohol . . .	3·89	2·86	..	1·66
Iso-butyl alcohol . . .	5·25	1·95		

In discussing his results, McLeod says that his values of the association factor " do not differ from those of other workers more than they differ amongst themselves," and the same remark applies to Bingham's figures. Comparison is difficult, as the determinations are all made at different temperatures

by the various authors.   McLeod says that his values refer to
0°, but this is hardly correct, as he uses the values corrected
to free space=0·1; Ramsay and Shields worked at 46°;
Bingham's values are obtained at temperatures of equal
fluidity=300, which differ widely, while Traube's data are
for room temperature.   McLeod's figures probably refer to
lower temperatures than any of the others, and may there-
fore be expected to be high.

McLeod summarises his views as follows: " If, then, the
association factors in column 6 can be considered justifiable,
it follows that the viscosity of a liquid is a linear function of
the molecular weight and varies inversely as the ' free space.'
Thorpe and Rodger in comparing liquids at their boiling-
points found constants for such groups as CH_2, Br, I, OH,
etc., depending on their chemical nature.   It follows from
the above statement that these groups have an influence
which depends only on their molecular weight, and not on
their contour, chemical nature, or position in the molecule.
Viscosity in liquids is, in fact, as in gases, due to a transference
of momentum, and does not depend on any property of the
molecule except its weight.   It is true the ' free space ' and
the degree of association may be governed largely by the
' chemical affinity ' between the molecules, but ' internal
friction ' in liquids is not itself a function of the surface
of molecules, and is not therefore analogous to the friction
between solid bodies."

McLeod is no doubt right in considering attempts to repre-
sent the mechanism of viscosity as friction between molecular
surfaces to be merely false analogies.   His views on the
respective effects of molecular weight and free space are
supported by the fact (cf. p. 71) that isomers showing different
viscosities also have different free spaces, the differences being
in the right direction.   On the other hand there are, as has
been pointed out in Chapters V and VI, considerable diffi-
culties in regard to the magnitude of the free space calculated
by his method, and the further one that the exponent A is
not actually =1, so that the relation between viscosity and
free space is not as simple as assumed.   Nevertheless, the
whole treatment of the subject is of great interest, and should

be capable of being developed further, if the effect of temperature at equal volume, and therefore equal free space, can be explained satisfactorily.

The investigations so far described start from some *a priori* assumption, like the additive character of viscosity (Thorpe and Rodger), or fluidity (Bingham), or the function of free space ·(McLeod). One or two purely empirical relations between viscosity and molecular constants must now be mentioned. The first of these, put forward by Dunstan,[12] is that the ratio η/molecular (volume) has low values not differing too much from the mean for non-associated liquids, while it is much higher for associated ones, and particularly those containing OH groups. A few examples will suffice.

Substance	$(\eta \times 10^6)/v$.	Substance.	$(\eta \times 10^6)/v$
Benzene . .	65	Acetone . . .	43
Ethyl acetate .	43	Water . . .	493
Carbon disulphide	60	Ethyl alcohol . .	189
Ethyl iodide .	69˙	Methyl alcohol .	138
Ethyl bromide .	51	Glycol . . .	2750
Toluene . .	53	Acetic acid . .	195
Chloroform .	67	Lactic acid . .	5410

Dunstan and Thole's Logarithmic Formula. A much more important relation found by Dunstan and Thole [13] is the logarithmic one:

$$\log \eta = a\mathrm{M} + b,$$

where M is the molecular weight, a is a general constant, and b is a constant characteristic for any one homologous series. The relation fails, like others, for the lower terms, especially of the fatty acid series, but holds well for a number of series. Table X gives the viscosity (in poises) of a variety of these at 20°, and the values of the logarithmic increment for the CH_2 group; for convenience the logarithms of $(\eta \times 10^5)$ are used:

TABLE X

INCREMENT OF $\log(\eta \times 10^5)$ FOR CH_2 (DUNSTAN and THOLE)

Substance.	η.	$\triangle \log(\eta \times 10^5)$ for CH_2.
Hexane . . .	0·00320	
Heptane . . .	0·00411	0·109 ⎫
Octane	0·00538	0·117 ⎬ 0·109 (paraffins).
Iso-hexane . . .	0·00300	0·102 ⎭
Iso-heptane . . .	0·00379	
Ethyl iodide . . .	0·00583	
Propyl iodide . . .	0·00737	0·102 ⎫
Iso-propyl iodide . .	0·00690	⎬ 0·102 (alkyl iodides).
Iso-butyl iodide . .	0·00870	0·101 ⎭
Methyl propyl ether .	0·002515	
Ethyl propyl ether . .	0·003175	0·101 ⎫
Propyl ether . . .	0·00420	
Ethyl ether . . .	0·002345	0·126 ⎬ 0·108 (ethers).
Propyl ether . . .	0·00420	
Methyl propyl ether .	0·002515	0·111
Methyl iso-butyl ether .	0·003065	
Ethyl iso-butyl ether .	0·003785	0·092 ⎭
Ethyl acetate . .	0·00449	
Propyl acetate . .	0·00581	0·112 ⎫
Methyl propionate . .	0·00454	⎬ 0·107 (esters).
Methyl butyrate . .	0·00575	0·103 ⎭
Acetone . . .	0·003225	
Methyl propyl ketone .	0·00501	0·096 ⎫
Methyl ethyl ketone .	0·00423	⎬ 0·106 (ketones).
Acetone . . .	0·00501	0·117 ⎭
Propyl alcohol . .	0·0226	
Butyl alcohol . . .	0·0295	0·116 ⎫
Iso-butyl alcohol . .	0·0391	⎬ 0·116 (alcohols)
Iso-amyl alcohol . .	0·0509	0·115 ⎭
Methyl sulphide . .	0·0293	
Ethyl sulphide . .	0·00455	0·091 ⎬ 0·091 (sulphides).

Mean value for 16 pairs = 0·107.

Dunstan and Thole then calculate the increments of log $(\eta \times 10^5)$ for the chief groups at 20°. One example will be sufficient. The value for hydrogen is found by subtracting from log $(\eta \times 10^5)$ for hexane, heptane, and octane respectively, 6, 7, and 8 ×0·107 (the average increment per CH_2), and dividing the difference by 2:

From hexane . 0·931.
From heptane . 0·932 (mean Δ log $(\eta \times 10^5)$ for H=0·934).
From octane . 0·938.

The values for other atoms and groups are:

OH (alcoholic) .	2·102	O (ethereal) .	0·098
CO (ketonic) .	0·407	C . . .	−1·761
Double bond .	1·847	Iso-union .	−0·030

The authors show that, by the use of these atom and group constants, it is possible to calculate the viscosity of even complicated compounds with fair accuracy. One example may be quoted:

Iso-butyl ethyl ether, η_{20}=0·00376 poises (T. and R.), $(CH_3)_2CH \cdot CH_2 \cdot O \cdot C_2H_5$ =

$$
\begin{aligned}
6CH_2 &= \quad 0·642 \\
O &= \quad 0·098 \\
2H &= \quad 1·868 \\
\hline
&\quad 2·608 \\
iso &= -0·030 \\
\hline
2·578 &= \text{log } (0·00378 \times 10^5).
\end{aligned}
$$

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[9] D. B. McLeod, *Trans. Faraday Soc.*, **21**, 151 (1925).

[10] W. Ramsay and J. Shields, *Trans. Chem. Soc.*, **63**, 1089 (1893).

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[12] A. E. Dunstan, *Zeit. physik. Chem.*, **51**, 738 (1909).

[13] Dunstan and Wilson, *Trans. Chem. Soc.*, **91**, 90 (1907); *cf.* also
Dunstan and Thole, *The Viscosity of Liquids*, pp. 31–38 (1914).

CHAPTER VIII

THE VISCOSITY OF SOLUTIONS

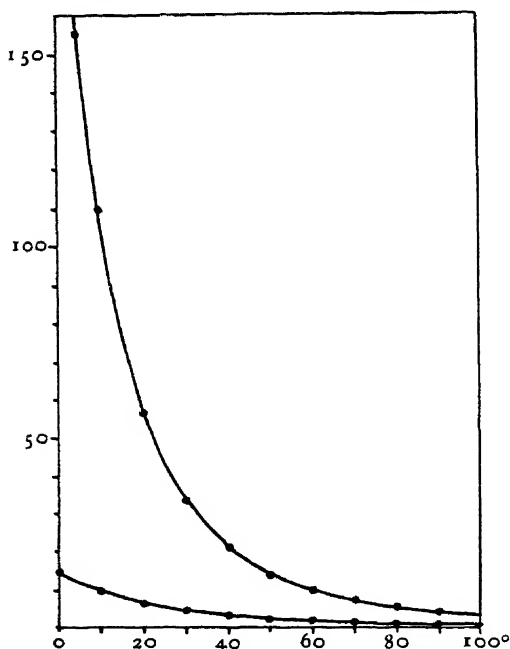**A. Non - Electrolytes.** The investigations on solutions of non-electrolytes are not numerous; the most extensively studied example is probably the solution of cane sugar (sucrose). Many of the earlier determinations, like those of Burkhardt,[1] Rudorf,[2] Grüneisen,[3] and Heber Green,[4] cover a small range of temperature only; Hosking,[5] however, measured the viscosity of solutions containing up to 40 per cent. by weight, at temperatures between 0° and 90°, with Thorpe and Rodger's instrument. The latest data are those of Bingham and Jackson,[6] who proposed this solution as a liquid suitable for calibrating viscometers.

FIG. 36.—Viscosity-temperature curves of 40 and 60 per cent. cane sugar solutions (Bingham and Jackson).

These are given in Table XI in centipoises, and the viscosities of the 40 and 60 per cent. solutions are plotted as ordinates against the temperatures as abscissæ in fig. 36.

TABLE XI

VISCOSITY OF SUCROSE SOLUTIONS (BINGHAM and JACKSON)

Temperature.	Grm. of sucrose in 100 grm. of solution.			
	0.	20.	40.	60.
0°	1·789	3·804	14·77	238
5	1·516	3·154	11·56	156
10	1·306	2·652	9·794	109·8
15	1·141	2·267	7·468	74·6
20	1·005	1·960	6·200	56·5
25	0·894	1·704	5·187	43·86
30	0·802	1·504	4·382	33·78
35	0·720	1·331	3·762	26·52
40	0·653	1·193	3·249	21·28
45	0·596	1·070	2·847	17·18
50	0·550	0·970	2·497	14·01
55	0·507	0·884	2·219	11·67
60	0·470	0·808	1·982	9·83
65	0·436	0·742	1·778	8·34
70	0·406	0·685	1·608	7·15
75	0·379	0·635	1·462	6·20
80	0·356	0·590	1·334	5·40
85	0·334	0·550	1·221	4·73
90	0·315	..	1·123	4·15
95	0·298	.	1·037	3·72
100	0·282	..	0·960	3·34

The great increase of viscosity with concentration at low temperature, and the rapid decrease in viscosity with temperature at high concentration, are both strikingly illustrated by this graph. The temperature coefficient, or, more precisely, the percentage decrease of viscosity per degree in the interval from 18° to 25°,

$$a = \frac{\eta_{18} - \eta_{25}}{25 - 18} \times \frac{200}{\eta_{18} + \eta_{25}},$$

has been calculated by Heber Green for the following concentrations (C = mols./litre) :—

C =	0·0	0·1	0·2	0·4	0·6	0·8	1·0	1·2	1·4
a =	2·390	2·454	2·520	2·637	2·778	2·945	3·117	3·345	3·707

C =	1·6	1·8	2·0	2·2	2·5	2·7
a =	4·10	4·47	4·90	5·58	6·48	7·20

8

An important distinction between solutions of non-electrolytes and of electrolytes shows itself in the relative viscosities at different temperatures, *i.e.* the ratios:

$$\frac{\eta \text{ of solution at temperature } t}{\eta_0 \text{ of solvent at temperature } t}.$$

The values for the 60 per cent. sugar solution are as follows:—

Temp.°	0	10	20	30	50	70	90	100
η/η_0 .	133·0	83·9	56·2	47·1	25·4	17·5	13·1	11·8

The relative viscosity, referred to water at the same temperature, decreases with rising temperature. We shall find later—as Ranken and Taylor [7] seem to have pointed out for the first time—that the reverse holds good for electrolyte solutions.

It is of interest to note that the volume change caused by dissolving sugar in water is not great. Green gives the following data for the molecular volume (*i.e.* volume of one grm.-mol.): solid 215·6 c.c., at extreme dilution 210·0 c.c., and at high concentrations 220 c.c.

The empirical formulæ expressing the variation of viscosity with temperature do not appear to have been applied to solutions. The author has tested Batschinski's relation (p. 76) by Bingham and Jackson's data for the 60 per cent. solution; the free space at 0°, calculated from the volumes and viscosities at 0° and 50°, amounts to only 0·123 per cent. of the total volume, and the viscosity at 25° calculated on this basis is about half the observed value.

The problem of finding a connection between concentration and viscosity has received much more attention, though there has been one attempt only at rational treatment, by Einstein.[8] This will be more conveniently discussed in the chapter on Colloidal Solutions; here it is sufficient to say that Einstein finds a linear increase in viscosity with concentration, a result which does not agree with observation except at very low concentrations. A number of empirical formulæ have been proposed, the most useful of which is that of Arrhenius: [9]

$$\eta/\eta_0 = A^c, \quad \text{or} \quad \log (\eta/\eta_0) = c \log A,$$

in which η_0 is the viscosity of the solvent, η that of the solution with the concentration c, and A a constant.

The concentration in this formula has been expressed in every possible way: volume of solute in volume of solution; weight of solute in volume of solution; molar ratio; mols. of solute in a fixed number of mols. of solvent, and mols. of solute in a fixed weight of solvent.

As regards the sugar solution, Heber Green found that the formula did not hold for concentrations above 0·2 mols./litre when expressed either as mols./litre or as volume of solute per unit volume of solution. He obtained the best agreement when using for c the value $c = v/w$, in which v is the volume of sugar and w that of water in unit volume of solution; varying discrepancies arose according as the molecular volume of sugar or that of water was assumed to remain constant.

Dunstan and Thole [10] find very good agreement between Green's experimental values and those calculated from Arrhenius's formula when the concentration is expressed in mols./1000 grm. of water. Below are given the values of A found in this way, the constancy of which is satisfactory.

Mols. of sucrose per 1000 grm. of water.	η (centip).	A
0	0·8953	
0·4382	1·3083	2·38
0·9666	2·105	2·42
1·618	3·805	2·44
2·440	7·973	2·45
3·516	20·72	2·44
5·440	105·8	2·41

Applying the same method of calculation to Bingham and Jackson's data, the author finds fair agreement at 20° but considerable discrepancy at 0°.

Table XI shows that the viscosity of sugar solutions at all concentrations and temperatures is higher than that of water, and this is the general rule with non-electrolytes. There are, however, instances of the phenomenon, which has been called

—not very felicitously—"negative viscosity" in electrolyte solutions, and held to be an exclusive characteristic of such, viz. lowering of the viscosity of the solvent by a solute. One example is p-nitrotoluene in ethyl alcohol, given by Wagner and Mühlenbein,[11] whose data are given below. C is the concentration in mols./litre, ρ the density, and η the relative viscosity, that of alcohol being taken as $=1$.

p-Nitrotoluene in Ethyl Alcohol

C.	ρ.	η.
1/1	0·83733	0·9989
1/2	0·81563	1·0039
1/4	0·80421	1·0018

The viscosity of the molar solution is smaller than that of the solvent—though the difference is probably not much greater than the experimental error—and it is obvious that the η-C curve has a maximum between $C=1$ and $C=1/2$. In view of the next example to be quoted—urea in water— it is unfortunate that no determinations at other temperatures are available.

Solutions of urea were investigated by Rudorf,[12] who found the viscosity lower than that of water. Fawsitt,[13] working with specially pure material, was unable to confirm this result. Ranken and Taylor (*loc. cit.*) again investigated this solution, and found its viscosity at all concentrations higher than that of water at 25°; at 8°, however, the viscosity of a solution containing 0·03125 mols./litre was found to be 0·9985 (η water $=1$).

It is worth pointing out that the density of the nitro-toluene solution increases continuously with concentration, as viscosities of liquid mixtures (*q.v.*) lower than that of either component are frequently ascribed to volume changes.

As regards the sugar solution, conditions are no doubt complicated by the association of the solvent and by hydration of the sugar molecules. Porter [14] has deduced hydration numbers, *i.e.* the number of molecules of water associated with one molecule of sugar, on the assumption that a formula of the type $P(v-b)=RT$ represents osmotic pressure;

if b is calculated from the experimental data it is found to be greater than the volume occupied by the sugar, and the difference is assumed to be due to water of hydration. In this way Porter finds that hydration decreases with increasing concentration and with rising temperature; at a concentration of 90·1 grm./litre the hydration number is 10·3 at 0° and 3·5 at 60°, while at a concentration of 256·7 grm./litre it is 5·5 at 0° and 3·3 at 60°. If either the mass or the volume of the hydrated molecule is the factor which determines the viscosity, the decrease of this volume or mass is in agreement with the fact which has been demonstrated above: that η/η_0 decreases with rising temperature, or, in other words, the viscosity of a sugar solution decreases at a more rapid rate than that of water.

"*Ideal*" *Solutions.* In view of these complicating factors it would be very desirable to have data on ideal solutions; unfortunately, the only determinations available were made at a single temperature. These are measurements on solutions of naphthalene and of diphenyl in benzene and in toluene, carried out at 25° by Kendall and Monroe.[15] The freezing-point of the benzene solutions has been determined over the whole range of concentrations used and found in agreement with the ideal solution law; a number of freezing-points have been determined for the toluene solutions and coincide with those for benzene, so that these solutions may also be assumed to be ideal ones. The investigation was undertaken with the object of testing the empirical formulæ connecting viscosity with concentration: all of them, including Arrhenius's, failed to represent the results. Kendall and Monroe applied a relation which gives good results for mixtures of indifferent non-associated liquids:

$$\eta^{1/3} = x\eta_1^{1/3} + (1-x)\eta_2^{1/3},$$

in which η, η_1, and η_2 are respectively the viscosities of the mixture and of the two components, and x is the molecular percentage of one of them. The formula was tested for solutions—where η_2, the "viscosity" of the solute, is of course unknown—by calculating η_2 from the experimental data. The results are given in Table XII.

TABLE XII

VISCOSITY OF IDEAL SOLUTIONS IN CENTIPOISES (TEMP. 25°)
(KENDALL and MONROE)

Per cent. of solute in solution.			η (obs.).	η_2 (calc.).
Weight.	Volume.	Molecular.		
Naphthalene in Benzene.				
0·0	0·0	0·0	0·6048	
8·11	7·3	5·10	0·6565	2·20
17·16	15·2	11·21	0·7261	2·30
22·97	20·6	15·38	0·7707	2·23
28·82	25·8	19·29	0·8263	2·27
34·10	30·8	23·98	0·8764	2·24
37·69	33·9	26·93	0·9178	2·27
			Mean	2·25
Diphenyl in Benzene.				
0·0	0·0	0·0	0·6051	
18·08	15·8	10·06	0·7585	3·41
30·57	27·3	18·24	0·9014	3·40
53·03	48·9	36·38	1·298	3·51
			Mean	3·44
Naphthalene in Toluene.				
0·0	0·0	0·0	0·5526	
5·73	4·8	4·19	0·5848	1·81
13·72	11·8	10·26	0·6394	1·80
20·12	17·4	15·33	0·6866	1·83
27·31	24·1	21·27	0·7470	1·86
			Mean	1·825
Diphenyl in Toluene				
0·0	0·0	0·0	0·5520	
21·38	18·6	13·98	0·7335	2·75
32·02	28·2	21·97	0·8587	2·81
38·97	34·8	27·61	0·9627	2·89
			Mean	2·82

It will be seen that for any one system the constancy of η_2 is satisfactory. The values of η_2 for either solute, calculated from the data for benzene solutions, are, however, different from the corresponding values for toluene solutions, so that

the physical meaning of η_2 (viscosity of " liquid naphthalene " at 25°; melting-point 80·5°) is quite obscure. The authors point out that the ratio, (η_2 from benzene data)/(η_2 from toluene data), is practically identical for both solutes, viz. 1·23 for naphthalene and 1·22 for diphenyl. While this agreement is interesting, it is difficult to see any physical meaning in it, or to consider the cube-root formula as anything but a further interpolation formula.

B. Electrolytes. Investigations on this subject have been extremely numerous since G. Wiedemann [16] suggested a connection between the viscosity and conductivity of salt solutions and made determinations of the viscosity coefficient. References to some of the earlier papers are quoted at the end of this chapter. A fresh impetus was given to the study of the subject by the development of the electrolytic dissociation theory; Arrhenius [17] himself carried out numerous measurements with an early form of the Ostwald instrument, and represented the results by the experimental formula already mentioned. A few general characteristics of electrolyte solutions may be summarised as follows:—

All electrolytes, with the exception of some salts of potassium, rubidium, cæsium and ammonium, increase the viscosity of water (or other solvent). The change in viscosity is not great for concentrations of several mols./litre, as shown by the data in Tables XIII to XVI; thus the viscosity of a lithium nitrate solution containing 5·849 mols. in 1000 grm. of solution is only little more than three times that of water at 25·01°. A few highly soluble salts, however, give very viscous solutions at high concentrations, such as calcium chloride, and particularly zinc chloride (Table XVII).

TABLE XIII

RELATIVE VISCOSITIES OF LITHIUM NITRATE SOLUTIONS (APPLEBEY)

η_0=viscosity of water at same temperature.
C=mols. in 1000 grm. of solution.

0°.		18°.		25·01°.	
C.	η/η_0.	C.	η/η_0	C.	η/η_0
0·0401	1·0032	0·00724	1·00124	0·0174	1·0026
0·0883	1·0058	0·0131	1·00200	0·0299	1·0040
0·1026	1·0076	0·0379	1·0047	0·0567	1·0067
0·2294	1·01545	0·0784	1·00905	0·0825	1·0099
0·4179	1·0278	0·1446	1·01545	0·1071	1·0125
0·4818	1·0325	0·2653	1·0278	0·2333	1·0267
0·8577	1·0616	0·7034	1·0737	0·3238	1·0354
1·134	1·0875	1·283	1·14395	0·3643	1·0405
1·572	1·1345	1·471	1·1699	0·5385	1·0597
2·099	1·2007	2·528	1·3498	0·8666	1·0980
2·508	1·2770	2·550	1·3579	0·9663	1·1112
		3·120	1·4906	1·316	1·1567
		3·279	1·5367	2·2719	1·3151
		4·363	1·9346	3·8541	1·74075
				4·578	2·0577
				5·849	3·0255

TABLE XIV

RELATIVE VISCOSITIES OF CÆSIUM NITRATE SOLUTIONS (MERTON)

η_0=viscosity of water at same temperature.
C=mols. in 1000 grm. of solution.

0°.		10°.		18°.		25°.
C.	η/η_0.	C.	η/η_0.	C.	η/η_0	η/η_0.
0·02513	0·9960	0·0292	0·9970	0·4529	0·9986	0·9988
0·05120	0 9901	0·0532	0·9932	1·0060	0·9660	0·9970
0·07609	0·9841	0·1609	0 9786	2·1415	0·9899	0·9926
0·09958	0·9793	0·2783	0·9625	3·1299	0·9844	0·9882
0·1984	0·9602	0·4196	0·9454	5·0677	0·9752	0·9811
0·2863	0·9941	0·5527	0·9309	6·5882	0·9681	0·9761
0·3965	0·9244	0·6423	0·9211	9·6569	0·9561	0·9671
				12·3740	0·9470	0·9604
				16·6355	0·9347	0·9518

TABLE XV

VISCOSITY OF ELECTROLYTE SOLUTIONS IN CENTIPOISES
(HERZ and MARTIN)

Solute Grm. in 100 c.c.	NaCl 26·694.	Na₂SO₄ 11·120	K₂SO₄ 10·962.	KI 39·006.	KI 12·020.	Oxalic acid 8·552.
Temperature 20°	1·835	1·410	1·136	0·888	0·951	1·193
,, 30	1·471	1·124	0·934	..	..	0·951
,, 40	1·211	0·922	0·771	0·635	0·647	0·780
,, 50	1·020	0·772	0·648	..	..	0·654
,, 60	0·877	0·659	0·571	0·493	0·481	0·561
,, 70	0·767	0·573	0·501	..	..	0·489
,, 80	0·681	..	..	0·398	0·374	0·430
,, 90	0·634	..	0·403	..	..	0·382

TABLE XVI

VISCOSITY OF AMMONIUM SULPHATE SOLUTIONS IN CENTIPOISES
(GRUNERT)

Concentration.	3·5 N.	1·75 N.	0·875 N.	0·4375 N.
Temperature 20°	2·394	1·455	1·196	1·088
,, 40	1·644	0·994	0·766	0·713
,, 60	1·203	0·730	0·551	0·512
,, 80	0·937	0·571	0·424	0·395

TABLE XVII

VISCOSITY OF CALCIUM CHLORIDE AND ZINC CHLORIDE SOLUTIONS

CaCl₂ at 20°.		ZnCl₂ at 25°.		
Grm. per litre.	η (centip.).	Per cent. by weight.	Grm.-equiv. per litre.	Relative vis- cosity (η/η_0)
0	0·9974	74·87	22·8	153
204·2	1·704	68·43	19·3	33·7
321·3	2·542	61·72	16·1	12·7
415·9	3·817	56·22	13·1	6·91
473·4	4·946	49·55	11·3	4·51
504·2	6·143	44·20	9·57	3·41
542·5	7·603	36·75	7·40	2·50
575	9·733	28·71	5·38	2·00
		22·17	3·92	1·67
		18·36	3·15	1·546
		12·22	2·51	1·372
		6·14	0·95	1·202
		3·08	0·46	1·108

Sodium hydroxide, which has been very carefully studied by Bousfield and Lowry,[18] also exhibits high viscosity at higher concentrations, as appears from the figures in Table XVIII, and the viscosity-concentration graph, fig. 37. Although the volume relations in solutions are obscure, the great contraction which occurs when sodium hydroxide is dissolved in water deserves mention. As the authors point out, 100 grm. of NaOH can be dissolved in 1 litre of water without an increase of volume, while 50 grm. produces a contraction of 3 c.c.

TABLE XVIII

RELATIVE VISCOSITIES AND FLUIDITIES OF SODIUM HYDROXIDE
SOLUTIONS AT 18° (BOUSFIELD and LOWRY)

Concentration.		η.	φ.
Per cent.	Mols./litre.		
0·0	0·0	1·00	1·0
2·50	0·64	1·08	0·923
7·68	2·08	1·43	0·700
14·28	4·15	2·25	0·444
20·14	6·13	3·84	0·260
25·0	7·94	6·69	0·145
30·2	10·03	11·81	0·0847
35·0	12·05	20·6	0·0485
40·0	14·29	32·3	0·0310
45·0	16·60	48·2	0·0207
50·6	19·37	74·7	0·0134

The viscosity of electrolyte solutions, like that of other liquids, decreases with rising temperature, but does so less rapidly than that of water, so that the *relative viscosity, referred to water at the same temperature, increases with rising temperature.* As has already been stated, the change is in the opposite direction in solutions of non-electrolytes. Table XIX gives η/η_0 for a number of salt solutions; the figures show that the rule holds equally for salts which raise and for those which lower the viscosity of water. It is therefore possible

that solutions of salts which, at ordinary temperature and concentration, increase the viscosity of water, may at a suitable concentration and sufficiently low temperature show an $\eta/\eta_0 = 1$, and at still lower temperature even < 1; a possibility pointed out long ago by Arrhenius.[19]   This case has
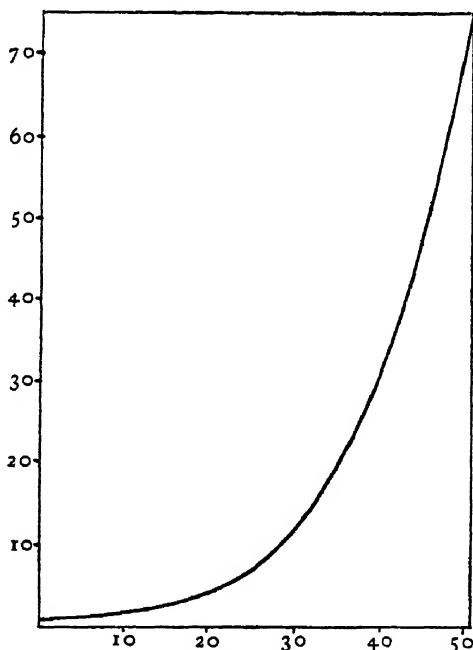
FIG. 37.—Viscosity-concentration curve of sodium hydroxide solution at 18° (Bousfield and Lowry).

not been realised experimentally.   Although data are available for the viscosity of concentrated (7·252 mols. in 100 mols. of water) calcium chloride solutions [20] down to a temperature of $-49\cdot16°$, they cannot be utilised, as the expression η/η_0 has no meaning below the freezing-point of the solvent. The point, which is of considerable interest, could be decided by investigating the viscosity of solutions in a dissociating solvent of low freezing-point like alcohol.

[TABLE XIX

TABLE XIX

η/η_0 OF ELECTROLYTE SOLUTIONS

Electrolyte	NaCl.	K$_2$SO$_4$.	KI.	(NH$_4$)$_2$SO$_4$	
Grm. in 100 c.c. of sol.	26·694.	10·962.	39·006.	23·10.	11·55.
Temperature 20°	1·826	1·130	0·883	2·382	1·447
,, 30	1·833	1·164			
,, 40	1·856	1·180	0·970	2·517	1·522
,, 50	1·854	1·163			
,, 60	1·866	1·214	1·049	2·538	1·553
,, 70	1·883	1·248			
,, 80	1·912	..	1·263	2·632	1·603
,, 90	2·012	1·279			

From Herz and Martın's data. — From Grunert's data.

Electrolyte, conc. 1 mol./litre.	NaCl.	KCl.	RbCl.	NH$_4$Cl
Temperature 5°	1·065	0·9307	0·9182	0·9637
,, 10	1·076	0·9464	0·9326	0·9464
,, 15	1·069	0·9588	0·9474	0·9553
,, 20	1·084	0·9751	0·9632	0·9682
,, 25	1·092	0·9866	0·9787	0·9765
,, 30	1·108	0·9975	0·9850	0·9900

From Sımon's data.[32]

The converse, of course, holds for salts which, over a certain range of concentration and temperature, lower the viscosity of water: at a suitable concentration and sufficiently high temperature η/η_0 should become $=1$, and at still higher temperature >1.   There is experimental evidence that this range is reached, *e.g.*, with potassium iodide, the concentration-viscosity curves for which have been determined at four temperatures, 10°, 18°, 30°, and 50°, by Getman [21] (fig. 38).   The

dotted lines show the viscosity of water at the same tempera-
tures and intersect the viscosity-concentration curves, except
that at 10°; in other words, at every temperature there is a
concentration at which
the viscosity becomes
equal to that of water.
At 10° this has not been
reached, although the
solubility would have
permitted it. The same
behaviour is shown by
ammonium salts, the vis-
cosity of which has also
been measured by Get-
man [22] at one tempera-
ture, 25° (fig. 39); with
the chloride and the
nitrate a concentration
is reached at which the
viscosity becomes equal
to that of water, and
there is no doubt that
the same thing would
happen with the bromide
and iodide at higher
temperature.

The salts producing
" negative viscosity " are
thus seen to conform to
what appears to be the
general rule for electro-

FIG 38.—Viscosity of aqueous solutions of
potassium iodide (Getman). Absc grm
in 100 c c of solution.

lytes, viz. their η/η_0 decreases with falling temperature, and
their peculiarity is merely that this ratio becomes smaller than
unity at easily attainable concentrations and temperatures.
They have, however, been the subject of many investigations
and theoretical speculations, which may be conveniently dis-
cussed at this place.

" Negative " Viscosity. The fact that some salts of potas-
sium, rubidium, cæsium and ammonium lower the viscosity

of water was discovered by Wagner.[23] A number of these salts were again investigated by H. C. Jones and his collaborators, as well as by Getman, while solutions of cæsium nitrate were studied over a wide range of concentrations and
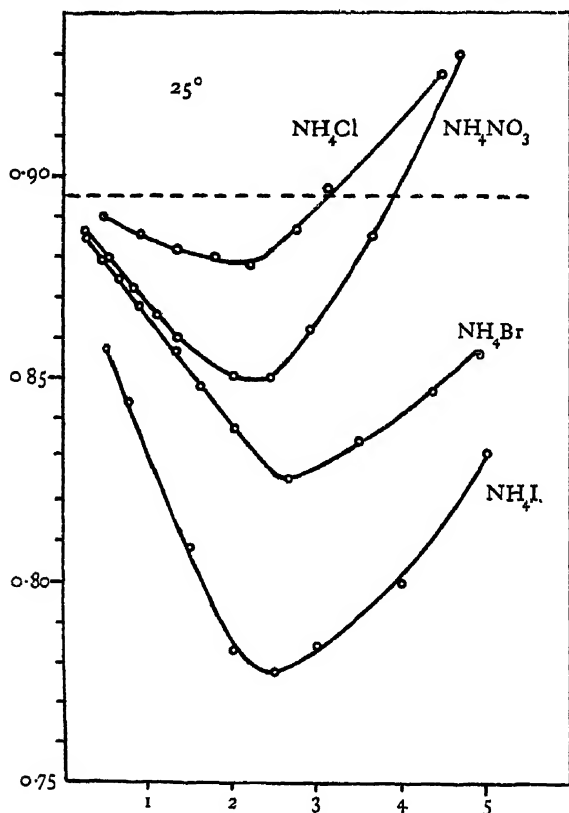
FIG. 39.—Viscosity of aqueous solutions of ammonium salts (Getman). Absc grm.-equivalents per litre.

the temperature interval from 0° to 25° by Merton.[24] Getman's data on potassium iodide and various ammonium salts have already been referred to (figs. 38 and 39). Merton's figures are given in Table XIV (p. 120) ; the concentrations are expressed as grm.-mols. in 1000 grm. of solution, and the viscosities as relative viscosities, η/η_0, referred to water at the same temperatures. The last two columns show η/η_0 at 18° and 25° for the same concentrations, so that they can be compared directly; η/η_0 is higher throughout at the higher tempera-

ture. At the highest concentration and temperature the relative viscosity is still <1, but linear extrapolation (which, judging from Getman's results with KI, gives too low a figure) from the interval 18° to 25° indicates that it should become =1 at about 54°.

Jones and Veazey [25] have put forward the following explanation of the lowering of viscosity by the salts mentioned above. The effects of anion and cation are additive, but while anions and undissociated salt always increase the viscosity, that of the cation depends on its atomic volume. The authors point out that potassium, rubidium and cæsium have the highest atomic volumes known; the volume of the NH_4 ion is of course unknown, but from its general chemical resemblance to K and Rb may be assumed to be high too. If a number of the small molecules of water are replaced by these large ions, the " frictional surface " is reduced and viscosity is lowered.

This picture of viscosity as friction between solid molecules, the whole surface of which, moreover, comes into play, a picture also used extensively by Thorpe and Rodger, is somewhat difficult to accept. As evidence that the substitution of a large number of small molecules for a small number of large ones increases viscosity, Jones and Veazey quote the mixtures of alcohol and water, which have viscosities considerably higher (see p. 142) than that of either component; both liquids are associated, and the degree of association of either is reduced by the presence of the other. The increase in viscosity on mixing is capable of other explanations, and that proposed by Jones and Veazey is inconsistent with the behaviour of water under pressure. As has been shown by Hauser, and again by Bridgman (p. 88), the viscosity of water at temperatures below about 30° is at first reduced by pressure, and the effect is quite generally attributed to depolymerisation, *i.e.* increase in the number of single molecules.

The question whether the lowering of viscosity is a specific effect of the cation is of course quite distinct from that just discussed, and Getman [26] has tried to obtain evidence on it by determining the viscosity of potassium iodide solutions in

various solvents in which the degree of ionisation is less than in water, viz. methyl alcohol, ethyl alcohol, ethylene glycol, glycerol, furfural, acetone, and pyridine. In fig. 40 the relative viscosities at 25° are plotted against the concentration in grm./100 grm. of solution for methyl alcohol, ethylene glycol, glycerol, and furfural; the concentrations attainable in the other solvents are too small for the scale adopted, but in all of them, viz. ethyl alcohol, acetone, and pyridine, potassium iodide increases the viscosity. The only solvent
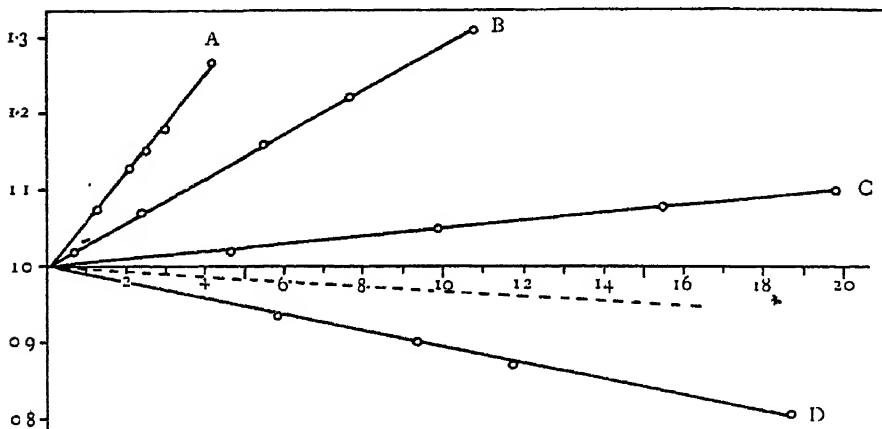
FIG 40.—Viscosity of potassium iodide solutions in organic solvents (Getman). A, methyl alcohol, B, ethylene glycol ; C, furfural, D, glycerol. Absc. grm. in 100 grm. of solution.

in which the viscosity is reduced is glycerol, and Getman suggests reasons for the view that ionisation is highest in this solvent. The decrease in relative viscosity is greater than in water, the values for which (at 30°, from Getman's data, fig. 38) are shown by the dotted line. Viscosity determinations on other salt solutions in glycerol have been carried out by Davis and Jones (*loc. cit.*, [11], Chapter III).

Getman's measurements at one temperature give no information on a point of great interest: whether the variation of relative viscosity with temperature in non-dissociating solvents would be the same as in electrolyte solutions, or whether KI in a non-dissociating solvent would behave like a non-electrolyte. In this connection an observation by Ranken and Taylor (*loc. cit.*, p. 114) is of great interest:

they find that mercuric cyanide, which is hardly ionised in aqueous solution, behaves like a non-electrolyte in this respect, *i.e.* $d(\eta/\eta_0)/dt$ is negative, as the following figures show:—

M/4	Temperature	$15°$	$25°$	$35°$	$45°$
$Hg(CN)_2$	η/η_0	1·0361	1·0345	1·0330	1·0310

The effect of the anion shows itself when the sulphates are compared with the haloid salts: potassium and ammonium sulphate raise the viscosity of water, although the chlorides and iodides lower it.

Taylor and Moore [27] question the cation effect, and more particularly that of the ionic volume. As regards the former, they compare potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$, and suggest that the ferro-salt, with four K ions, should produce a lower viscosity than the ferri-salt, with three. The reverse is, however, the case, as the following figures show:—

Viscosity in Centipoises at $25°$

Mols./litre.	$K_3Fe(CN)_6$.	$K_4Fe(CN)_6$.
0·50	0·00988	0·01120
0·25	0·00932	0·00996
0·125	0·00910	0·00944

As regards the ionic volume, the authors determine the viscosity of solutions of several of the quaternary ammonium salts. The volume of these ions is not known, but they must be considerably larger than the ammonium ion. Nevertheless, as the data in Table XX show, all the salts increase the viscosity of water.

TABLE XX

TABLE XX

(TAYLOR and MOORE)

m = grm.-mols. per 1000 grms. of water.
ϱ = density.
η/η_0 = relative viscosity referred to water at same temperature.

25°.			35°.		
$m.$	$\varrho.$	$\eta/\eta_0.$	$m.$	$\varrho.$	$\eta/\eta_0.$
		Tetra-methyl-ammonium Iodide.			
0·0685	1·0022	1·0042	0·1106	1·0019	1·0036
0·1300	1·0064	1·0060	0·1527	1·0050	1·0076
0·2550	1·0149	1·0124	0·1774	1·0065	1·0127
		Tetra-propyl-ammonium Chloride.			
0·2733	0·99520	1·2405	0·1772	0·99266	1·1350
0·2771	0·99529	1·2450	0·3324	0·99161	1·2600
0·6177	0·99433	1·6235	0·7884	0·99013	1·8030
0·7884	0·99425	1·8250			
		Tetra-ethyl-ammonium Chloride.			
0·2911	0·99713	1·0987	0·2935	0·99401	1·1076
0·5893	0·99755	1·2187	0·4747	0·99426	1·1760
0·7878	0·99815	1·3155	0·7509	0·99467	1·3000
1·148	0·99935	1·5255	1·0922	0·99570	1·4571

The authors point out the low density of these solutions, which, for tetra-propyl-ammonium chloride at 25°, is actually lower than that of water. It is of interest to consider this point, or more exactly the volume changes, in other solutions, since it is reasonable to assume some connection between the volume change and the viscosity change produced by dissolving a salt in water, even though the connection is not a simple quantitative one. Table XXI gives Happart's [28] data. δ is the contraction in c.c. produced when solid salt of density ρ is dissolved to form 100 c.c. of solution containing p per cent. The contraction is greatest for sodium chloride, which increases the viscosity of water, lower for potassium chloride, which lowers it between certain limits of concentra-

tion and temperature, and negative for ammonium chloride, which has the same effect as potassium chloride. More definite conclusions could be drawn if data for the contraction over an extended temperature range were available.

<div align="center">TABLE XXI</div>

CONTRACTION δ IN SALT SOLUTIONS CONTAINING p GRM. IN 100 C.C. (HAPPART)

NaCl. $\varrho=2\cdot23$.		KCl. $\varrho=1\cdot559$.		NH$_4$Cl. $\varrho=1\cdot559$.	
p.	δ.	p.	δ.	p.	δ.
1·03	0·22	1·76	0·278	1·87	−0·043
3·46	0·63	3·15	0·478	2·98	−0·071
3·61	0·65	4·65	0·663	3·44	−0·085
4·84	0·845	5·3	0·748	4·43	−0·153
4·95	0·86	6·34	0·88	4·87	−0·173
5·52	0·94	8·72	1·15	6·85	−0·216
8·50	1·40				

The variation of viscosity with temperature in solutions has not received as much attention as that in pure liquids. Herz and Martin [29] have tried to represent the fluidity of the salt solutions given in Table XV by Batschinski's formula (see p. 121):

$$\phi = (v - \omega)/c$$

(v specific volume, ω and c constants), and by a linear formula proposed by Meyer and Rosencranz : [30]

$$\phi = a + bT,$$

in which a and b are constants, and T is the absolute temperature. The agreement is, however, far from satisfactory, as the error is below 1 per cent. in two or three cases only, while it amounts to 7 and 8 per cent. in several others.

Anomaly of Electrolyte Solutions. A further peculiarity of electrolyte or, more precisely, salt solutions, discovered by

Grüneisen,[31] remains to be described.   He found for eighteen salts that the expression

$$\frac{\eta/\eta_0 - 1}{m}$$

(η/η_0 relative viscosity referred to water at the same temperature, m concentration in grm.-equivalents) had a *minimum*, whether the salt increased or reduced the viscosity.   Grüneisen considers that this effect, which has not been detected in solutions of non-electrolytes, is best explained by dissociation; the increase of the relative viscosity increment per grm.-equivalent at great dilution is most easily explicable on the assumption that dissociation of a molecule always causes an increase in viscosity.

Grüneisen then attempts to deduce a formula for the viscosity on the assumption that each species of ions increases the viscosity in linear ratio to its concentration, and that there is no mutual action, and arrives at the following expression:—

$$\frac{\eta/\eta_0 - 1}{m} = A\alpha + B(1 - \alpha) + Cm,$$

where A, B, and C are constants, and α the degree of dissociation.   In view of various simplifications in the deduction and the use of three constants, Grüneisen considers that this equation is not much more than an interpolation formula.   It was tested by introducing for α the value Λ_m/Λ_∞, the ratio of molecular conductivities at the concentration m and at infinite dilution, and fitted the experimental observations up to concentrations several times normal.   The observations at low concentrations are the most important for determining the coefficient A, which gives the increment in relative viscosity caused by one grm.-equivalent completely dissociated in one litre of water, assuming that there is no mutual action of the ions.   Grüneisen points out the fundamental difficulty in the way of verifying whether the effect of the ions is simply additive: that at the lowest concentrations at which the viscosity can be determined with sufficient accuracy dissociation is yet far from complete.

The minimum in the viscosity increment-concentration

curve has been confirmed by Applebey (*loc. cit.*, p. 43) for lithium nitrate, which increases the viscosity, and by Merton for cæsium nitrate, which lowers it. Fig. 41 shows one of Applebey's determinations, in which the viscosity increments, $(\eta/\eta_0 - 1)/m$, are plotted against $10^3 \times \sqrt{m}$, a method of representation adopted by Grüneisen to obtain " a practicable scale."

Applebey found that the results in very dilute solutions
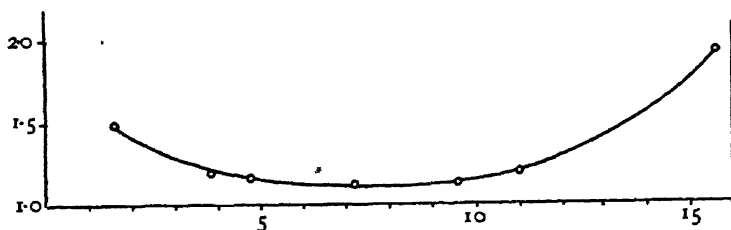
FIG. 41.—The anomaly of electrolytes (Applebey, after Grüneisen). Ord. $(\eta/\eta_0 - 1)/m$.   Absc. $10^3 \times \sqrt{m}$.

could not be represented with satisfactory agreement by Grüneisen's formula. He suggested an alternative which, apart from assumptions of the same kind as made by Grüneisen, contains factors that were, and still are, unknown, like the number of single and triple water molecules present, so that a discussion seems unprofitable.

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CHAPTER IX

THE VISCOSITY OF LIQUID MIXTURES

POISEUILLE [1] and Graham [2] already determined the times of transpiration of several liquid mixtures, and since then the subject has received constant attention. The extent of the experimental material accumulated can be realised from the number of references in the supplementary volume of Landolt and Börnstein's Tables (1927), which runs to about eleven hundred. These investigations have been undertaken with a variety of objects, which fall roughly into two classes: endeavours to find mathematical expressions connecting the viscosity of a mixture with those of the components and their ratio, and attempts to deduce changes in a mixture, such as alterations in the degree of association, or the formation of complexes or compounds, from peculiarities in the viscosity-ratio curves and their departure from laws assumed to hold good for ideal mixtures. The fundamental difficulty in the way of drawing any definite conclusions from an enormous mass of data is that the law of " ideal " mixtures is not known.

Empirical Formulæ. Kendall and Monroe [3] emphasise this point in a useful summary of the situation. The simplest assumption is that the viscosity of an ideal mixture should be additive:

$$\eta = \eta_1 x + \eta_2 (1 - x),$$

where η is the viscosity of the mixture, η_1 and η_2 are those of the components, and x the fraction of the first component present in the mixture. x has been expressed as a volume fraction, weight fraction and molar fraction, without justification for any one of these procedures. There are, however, no

mixtures which follow this linear law, in whatever way the concentration is expressed; the η-x curves which approach it most closely are slightly " sagged " or convex towards the x-axis, or, in other words, the viscosity of the mixture is lower throughout than that calculated from a linear formula.

Bingham [4] has put forward the view that it is not the viscosity but the fluidity which should be additive:

$$\phi = \phi_1 x + \phi_2 (1 - x).$$

This equation had previously been tested by Lees,[5] and found unsatisfactory when the concentration was expressed as a volume fraction; it is equally inadequate when weight fractions are used, as proposed by Drucker and Kassel.[6]

A purely empirical formula was proposed by Arrhenius,[7]

$$\eta = \eta_1^{x} \eta_2^{(1-x)}, \quad \text{or} \quad \log \eta = x \log \eta_1 + (1 - x) \log \eta_2,$$

so that the logarithms of the viscosities are assumed to be additive.

The logarithmic formula, when x is expressed as volume fraction, holds fairly well for mixtures containing up to about 0·1 of one component, but fails to represent the viscosity of a mixture over the entire range from $x=0$ to $x=1$. Kendall suggested expressing the concentration as molar fraction, which in many cases gives much closer approximation to experimental data. The formula, of course, applies equally to fluidity, as $\log \eta = -\log \phi$. (The modified form applied to solutions has already been mentioned, p. 114.)

Kendall and Monroe then proceed to test all the formulæ given above on eighty-four mixtures of presumably non-associated and chemically indifferent liquids. These give, in general, curves which, as has been mentioned, are slightly sagged; the more so the greater the difference in the viscosities of the components, whatever the way in which the concentration is expressed. The deviation from the straight line is generally least when this is done as molar fraction, and this method has been adopted in fig. 42, which shows three typical examples.

The figures below give the average divergence, the maximum divergence in either direction with its sign, and the " directional divergence," *i.e.* excess of divergences of one

sign over those of the opposite sign, averaged for all the eighty-four mixtures.   It is not easy to draw any conclusions from
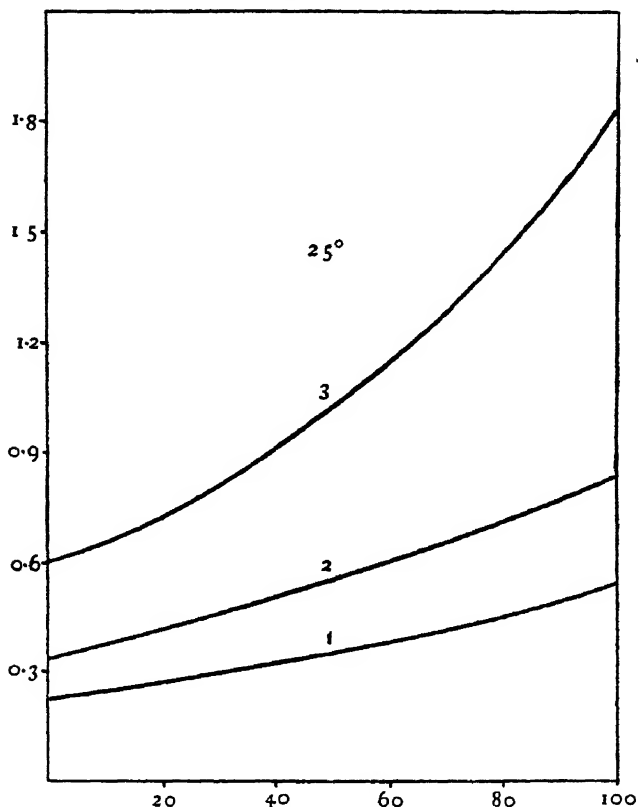
FIG. 42.—Viscosity of ideal mixtures (Kendall and Monroe). 1, Toluene-ethyl ether ; 2, decane-hexane at 25° ; 3, nitrobenzene-benzene. Absc. mols. per cent. of first component.

these figures, as it is always possible to ascribe divergences to deviations from the " ideal " character of any mixture.

	Divergence per cent.		
	Average.	Maximum.	Directional.
Linear viscosity, volume ratio .	11·1	+66	+10·2
Logarithmic viscosity, volume ratio	4·7	+27	+ 3·6
Linear fluidity, volume ratio .	3·4	−22	− 1·8
,, ,, weight ,, .	3·2	−15	− 0·1
Logarithmic viscosity, molar ratio	2·3	+ 8	+ 0·2

" Ideal " Mixtures.   Kendall and Monroe therefore endeavoured to find ideal mixtures, and more particularly such in which the components should have widely different viscosities and molecular weights.   Many of the earlier investigations dealt with pairs of components whose viscosities and molecular weights were not far apart, and this reduces the discrepancies caused by expressing the concentration in different ways.

One of the mixtures selected was benzene-benzyl benzoate.   Calorimetric measurements failed to show any evolution or absorption of heat on mixing; density determinations proved that there was no alteration of volume; and, finally, the depression of the freezing-point of benzene by benzyl benzoate was found normal. As regards the differences between the two liquids, the viscosity of the ester is about fourteen times that of benzene, its molecular weight about three times, while its density is about 30 per cent. higher.
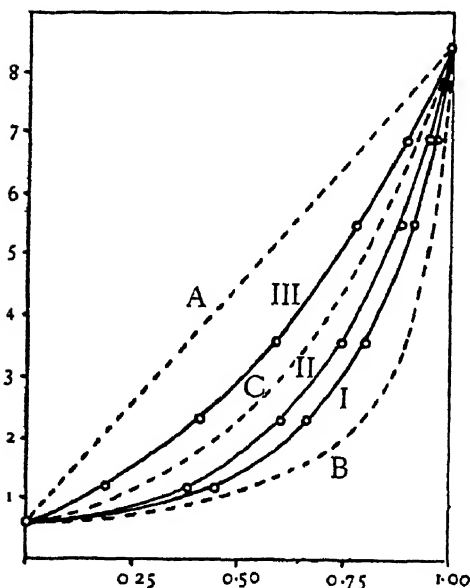
FIG. 43.—Viscosity of benzyl benzoate-benzene mixture (Kendall and Monroe).

Calculated.	Observed.
A = linear η.	I, weight fraction.
B = linear ϕ.	II, volume fraction.
C = logar. η.	III, molar fraction.

Fig. 43 shows in full lines the viscosity found experimentally plotted against the concentration of the ester expressed as I, weight fraction; II, volume fraction; and III, molar fraction.   The dotted lines give the viscosity calculated from A, the linear viscosity formula; B, the linear fluidity formula (which, as will be easily understood, fall on a hyperbola); and C, the logarithmic formula.

The experimental η-x curves differ widely according to the method chosen for representing the ratio, and none of them approach the curves calculated from the *a priori* equations.

The question then arises whether any other expression can be found for the viscosity of this mixture, which is as nearly as possible ideal. Kendall and Monroe find that this can be done by the cube-root formula already mentioned (p. 117):

$$\eta^{1/3} = x\eta_1^{1/3} + (1-x)\eta_2^{1/3},$$

in which x is the molar per cent. concentration of the ester. This equation very exactly represents the viscosity of the benzene-benzyl benzoate mixture, as well as of two similar systems, but it fails for a mixture of benzyl benzoate with toluene, as shown by the figures in Table XXII.

TABLE XXII

CALCULATED AND OBSERVED VALUES OF VISCOSITY OF TOLUENE-BENZYL BENZOATE MIXTURE (KENDALL and MONROE)

Per cent. of ester in mixture.			η (centip.).		Divergence per cent.
By weight.	By volume.	Molar.	Obs.	Calc.	
0·00	0·00	0·00	0·5520		
41·69	35·58	23·67	1·183	1·362	+15·1
63·11	56·93	42·61	2·015	2·399	+19·1
81·09	76·82	65·02	3·614	4·182	+15·7
89·60	86·94	78·90	5·086	5·645	+11·1
95·41	94·16	90·02	6·600	7·024	+ 5·5
100·00	100·00	100·00	8·450		

One may agree with Kendall and Monroe in finding the failure unexpected, and also in their conclusion that the cube-root formula may not have any theoretical foundation. They point out that an interpolation is the less likely to fit the experimental data the greater the difference between the viscosities of the components, and this difference is greatest for toluene and benzyl benzoate, $\eta_1 = 0.5520$, and $\eta_2 = 8.4500$ centip., or $1 : 15.3$. The ratio for benzene, $\eta_1 = 0.6044$, is 13.9, which possibly may be the maximum ratio for which the interpolation holds good. All that can be said for the cube-

root formula is that it represents the viscosity of mixtures approximately ideal, such as, *e.g.*, hexane-decane, measured by Bingham, better than any other.

Types of Viscosity-composition Curves. The author has thought it well to abandon the historical order and to begin the present chapter with an account of the investigation just described, because it shows quite clearly that the viscosity-concentration function for a mixture approaching the ideal as closely as possible is not known, but is certainly not linear. It is therefore obvious that all attempts to deduce changes in the molecular complexity or chemical composition of mixtures from peculiarities of the η-x curves and their deviations from an arbitrarily assumed linear law must be viewed with caution, unless there is independent evidence of such changes. The principal types of such curves may now be considered.

FIG. 44.

FIG. 45.

Relative viscosity of mixtures (Wagner).

FIG. 44.—Nitrobenzene and n-butyl alcohol.
FIG. 45.—Nitromethane and ethyl alcohol.

Absc. weight per cent. of nitro-compound.

Examples of the simple sagged curve, in which $d\eta/dx$ increases or decreases continuously, have already been given. Very frequently $d\eta/dx$ changes sign, *i.e.* the viscosity passes through a minimum, which—as need hardly be pointed out —is lower than the viscosity of either component, so that " negative viscosity " is fairly common in liquid mixtures.

Examples of such mixtures are nitrobenzene-n-butyl alcohol (fig. 44) and nitromethane-ethyl alcohol (fig. 45), measured by Wagner and Mühlenbein;[8] phenetole- and anisole-ethyl alcohol (fig. 46), measured by Baker.[9]

Curves showing Maxima. Curves concave to the concentration axis in which $d\eta/dx$ does not change sign are less common; very generally the viscosity has a maximum value. An example of this type is the mixture chloroform-acetone, the viscosity-concentration curves for which, at four temperatures, are shown in full lines in fig. 47. This should be considered in conjunction with fig. 48, which similarly gives the η-x curves (exhibiting a minimum) for the mixture acetone-carbon disulphide. Both are taken from an exhaustive investigation by Faust[10] of
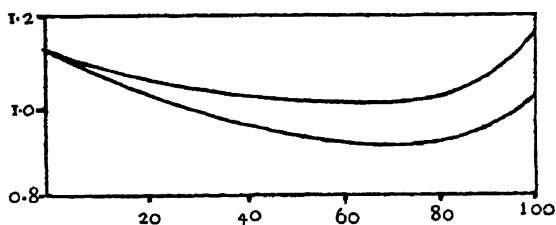
FIG. 46.—Viscosity of mixtures of phenetole (upper curve) and anisole (lower curve) with ethyl alcohol (Baker). Absc. volume per cent. of first component.

mixtures the vapour-pressure curves of which had previously been determined by Zawidzki.[11] Faust gives a complete bibliography of investigations on mixtures.

Faust points out that the ratio at which the maximum or minimum occurs is a function of the temperature; with rising temperature the maximum shifts more and more towards the viscosity of the more viscous component, and at the same time becomes less pronounced or disappears entirely. Conversely, in mixtures showing a minimum this shifts with rising temperature towards the viscosity of the less viscous component, and likewise tends to disappear. The effect in both types is that with rising temperature the viscosity approaches more and more the values calculated from the linear mixture formula. Incidentally this fact contradicts Bingham's assumption that the fluidities are additive, since the ϕ-x curve necessarily becomes more and more hyperbolic as the η-x curve approaches more and more to a straight line.

Very high maxima occur with mixtures of several organic liquids, like the alcohols and acetic acid, with water, which have been extensively investigated by Dunstan and Thole,[12] Getman,[13] and Bingham and Jackson.[14] Fig. 49 shows the viscosity-concentration curves of ethyl alcohol-water mixtures at four temperatures from the last-named authors' data. The curves flatten rapidly with rising temperature, but the maximum up to 40° remains practically at the same ratio, about 40 per cent. by weight of alcohol; at 60° the maximum lies at about 50 per cent. The curve for methyl alcohol-water (Getman) is almost straight at 60°. The curves for acetic acid-water (fig. 50) are very similar to those of the alcohol-water mixtures, with an even sharper maximum, which also remains at the same ratio over a certain range of temperature. Such maxima are always pronounced when there is contraction and evolution of heat on mixing, and when

FIG. 47.

FIG. 48.

Viscosity and vapour-pressure of mixtures (Faust).

FIG. 47.—Acetone-chloroform.
FIG. 48.—Acetone-carbon disulphide.

Ord. left, centipoises ; right, cm. of mercury.
Absc. volume per cent. of second component.

chemical combination must be presumed, as in mixtures of organic bases and acids.

Before considering special cases it is necessary to summarise the various attempts to explain the types of curves so far described. They all assume that deviations from a linear additive law, which ought to hold for " ideal " mixtures,
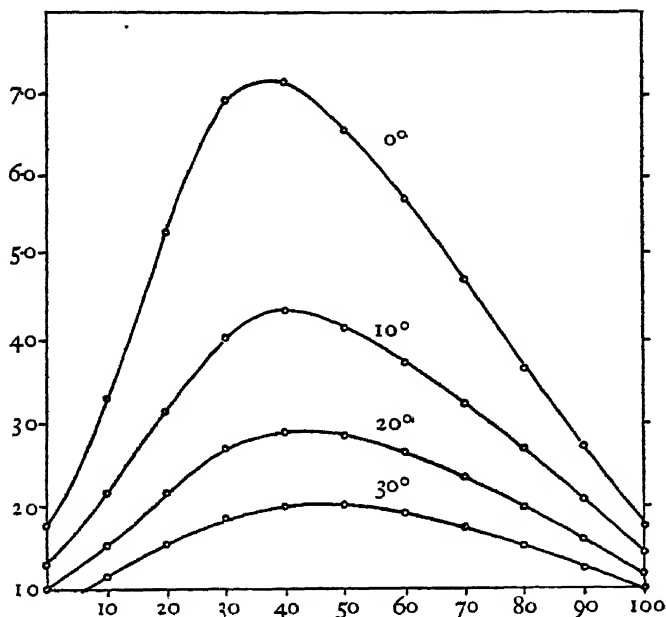
FIG. 49.—Viscosity of ethyl alcohol-water mixtures (Bingham and Jackson).   Absc. weight per cent. of alcohol.

are to be accounted for, although, as has been discussed above, and may, perhaps, be emphasised once more, there is no evidence that mixtures ideal in the accepted sense of the term behave in this simple manner.   Apart from this agreement, two diametrically opposed views have been put forward. Jones and Veazey (*cf.* p. 127) state that in a mixture of associated liquids each component reduces the degree of association of the other; the result is the formation of a larger number of simple molecules from a smaller number of large complexes, with an increase of " frictional surface " and a consequent increase in viscosity.   Apart from the diffi-culty of accepting this view of the mechanism of viscosity,

there are instances in which the viscosity-ratio curves of mixtures of highly associated liquids are deeply sagged, *e.g.* ethylene glycol-water (fig. 51), whereas Jones and Veazey's reasoning leads to the conclusion that they ought to exhibit maxima.

The opposite view is taken by Dunstan and his collabora-
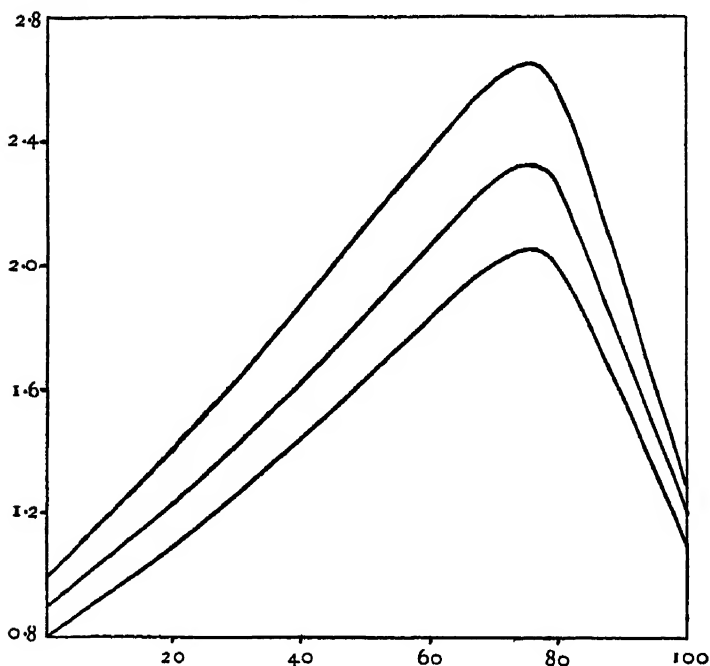
FIG. 50.—Viscosity of acetic acid-water mixtures (Dunstan), at 20°, 25° and 30°.   Absc. volume per cent. of acetic acid.

tors,[15] by whom a considerable portion of the experimental material has been provided.   Dunstan and Thole point out that, generally speaking, associated liquids—and particularly those containing hydroxyl groups—have relatively high viscosities, and therefrom conclude that a maximum in the viscosity curve indicates further association and eventually complex formation.   Sagged curves and minima are, on this basis, to be explained by dissociation—as, *e.g.*, the ethylene glycol-water curve (fig. 51) already quoted.

As mentioned, maxima are held to occur whenever there is chemical combination; it is questionable whether the con-

verse can be safely assumed that all maxima are due to the
formation of compounds or definite hydrates.   Graham (*loc.
cit.*, p. 135) was the first to make this assumption, and also
the further one that the ratio of the components at which
it occurred indicated the composition of the compound
formed.   It has later been postulated as criterion of com-
bination that the position of the maximum should be invariant
with temperature,[16] and that its displacement with tempera-
ture disproves the exist-
ence of, *e.g.*, definite
hydrates.   Dunstan and
Thole reply to this that
the hydrate may be so
labile that changes in
temperature or concen-
tration bring about a
displacement. This con-
flict of opinion is not
confined to viscosity
maxima, but extends
to the wider question
whether singularities in
any physical property
of mixtures are sufficient
proof of combination.[17]   In this connection it is of interest
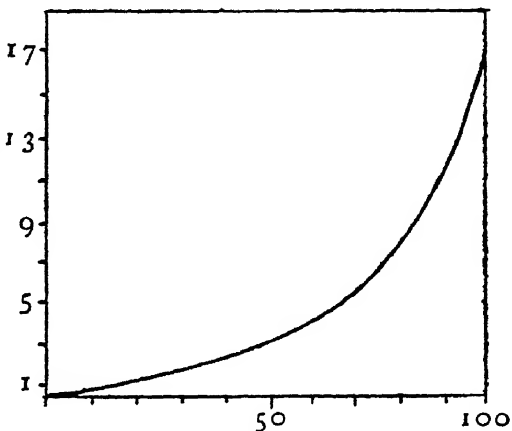
FIG. 51.—Viscosity of ethylene glycol-water
mixtures (Dunstan).   Absc. volume per cent.
of glycol.

to examine briefly a few cases in which two properties show
such singularities, viz. vapour pressure and viscosity.   The
existence of such a connection was first pointed out by Faust
(*loc. cit.*, p. 141), who found that mixtures having a viscosity
greater than that calculated from the linear formula had
vapour pressures lower than those calculated on the same
basis.   Examples are pyridine-acetic acid, aniline-acetic acid,
acetic anhydride-water, and chloroform-acetone.   The forma-
tion of compounds is practically certain in the first three
mixtures, and is probable in the fourth, as there is evolution
of heat on mixing.   The opposite behaviour is shown by
carbon disulphide-acetone, which has a viscosity minimum
at low temperature and a maximum on the vapour-pressure
curve.

Singularities in Viscosity and Vapour-pressure Curves. In figs. 47 and 48 the vapour-pressure curves determined by Zawidzki (*loc. cit.*) at 35·17° are plotted in dotted lines. The nearest temperatures at which the viscosity was determined were 39° for the acetone-chloroform mixture and 35° for the acetone-carbon disulphide mixture. At these temperatures the maximum in the first, and the minimum in the second, set of curves has entirely disappeared, so that no comparison regarding the position, and therefore of the complex causing the maximum and minimum, is possible. The pyridine-water system behaves anomalously, inasmuch as both the viscosity and the vapour-pressure curves have maxima. This is probably explained by the formation of a compound in the liquid, which is dissociated to the extent of about 96 per cent. in the vapour.[18]

Yajnik and collaborators[19] have examined a number of further mixtures the vapour pressures of which were determined by Zawidzki, and generally confirm Faust's results— viz. mixtures having a practically linear viscosity curve have a similar vapour-pressure curve (*e.g.* benzene-bromobenzene); a maximum in the viscosity curve corresponds to a minimum in the vapour-pressure curve, and *vice versa*. They also find incidentally that Porter's relation between the temperatures, at which two liquids have equal viscosities (see p. 74), holds equally for two mixtures.

Kendall and Monroe, in the paper quoted above, also refer to the parallelism between viscosity and vapour-pressure curves; there are three types of each, and the same explanations are applied to the two anomalous ones. The parallel, however, fails in the most important point, as the ideal mixture curve for viscosity is almost certainly not a straight line.

There is fairly general agreement that the particular ratio at which a viscosity maximum occurs does not necessarily, or even probably, indicate the composition of the compound or complex causing the maximum. It has been suggested by Findlay,[20] and again by Denison,[21] that it is not the position of the maximum, but the maximum deviation from the ideal mixture law, which is the important factor. This

maximum deviation, however, is necessarily unknown as long
as the law of ideal mixtures is unknown; and again to assume
a linear law does not bring the problems involved any nearer
a solution.   Furthermore, unless the whole or the greater
portion of the components combines or associates, the mixture,
as Denison points out, is a solution of the compound or
complex formed in a mixture of the uncombined components,
and therefore a ternary mixture.   In view of our ignorance
of the true law of binary mixtures it seems rash to attempt
any interpretation of the behaviour of mixtures of more than
two components, with the additional handicap that the con-
centrations are not known.

On the other hand, as Dunstan and Thole point out, the
position of the maximum will coincide with the composition
of the compound or complex if the whole, or the greater
portion, of the components combine, and if the viscosity of
the complex is greater than that of one or both components.
It is of course possible, as suggested by Baker, that a complex
may have a lower viscosity than that of one or the other
component, in which case the curve should have a minimum.
There is, however, no indication of it in the case contemplated
by him (ether-alcohol).

Viscosity Maxima and Compound Formation.   The com-
parative simplicity of viscosity determinations is naturally a
temptation to employ them for demonstrating combination in
mixtures.   Numerous investigations intended to demonstrate
this possibility have accordingly been carried out on binary
mixtures for which there is independent evidence of such
combination.   Among the earliest is one by Tsakalatos,[22]
who studied mixtures of (1) m-cresol with aniline and with
o-toluidine (fig. 52).   Both curves show a very marked
maximum at a ratio of about molar 65 per cent. of m-cresol
to 35 of the other component.   The fusion curves determined
by Kremann [23] demonstrate the existence of a compound of
one molecule of m-cresol with one molecule of aniline or of
o-toluidine.   The displacement of the maximum in the vis-
cosity curve is explained by the ternary character of the
system, which consists of the inactive binary mixture and the
compound which would be present in maximum amount at

the ratio 50: 50, and shifts the maximum towards the side of the component having the higher viscosity.

(2) Acetone and Chloroform. The curves for this mixture, determined by Faust and illustrated in fig. 47, have already been discussed. Tsakalatos considers that there is evidence of a compound of one molecule of acetone with one of chloroform, the quantity formed increasing with falling temperature. The viscosity curve at —13° has a maximum at about 65 mols. per cent. of chloroform, which shifts in the usual manner towards that of the more viscous component with rising temperature, and finally disappears.
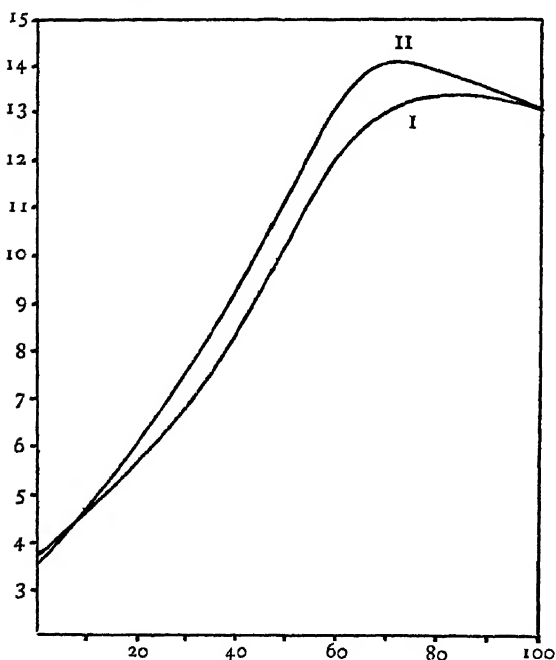
FIG. 52.—Viscosity of mixtures of meta-cresol and (I) aniline; (II) o-toluidine (Tsakalatos). Absc. mols. per cent. of m-cresol.

(3) Pyridine and Acetic Acid (fig. 53). There is considerable evidence of the formation of a compound of two molecules of pyridine with three of acetic acid. The viscosity maximum occurs at about 78 (instead of 60) mols. per cent. of acid, while there is a density maximum at about 86 per cent. Butyric acid and pyridine combine in the same ratio, and the viscosity curve has a maximum at about 72 per cent. of acid, while the maximum density falls almost exactly at the molar ratio of the compound, 60 per cent. of acid. The maxima in both curves are, as usual, displaced towards that of the more viscous component.

A number of peculiar systems have been studied by Kurnakow and his collaborators,[24] who do not consider maxima which shift with temperature sufficient evidence of

the formation of definite molecular compounds.   They again compare the conditions in such mixtures with those causing maxima and minima in vapour-pressure curves.

Kurnakow finds a new type of graph characteristic of binary mixtures containing a definite compound.   This consists of two branches convex to the concentration axis, which intersect at an angle at the maximum point; the maximum is independent of temperature, and its position corresponds to the composition of the compound.   For obtaining curves of this type it is necessary to choose binary mixtures which, when the reaction has occurred, still remain liquid and homogeneous.

A reaction which Kurnakow and Shemtchushni find particularly suitable is that between the thiocarbimides (mustard oils)

FIG. 53.—Viscosity of mixtures of pyridine and (lower curve) acetic (upper curve) butyric acid (Tsakalatos).   Absc. mols. per cent. of pyridine.

and secondary amines, which leads to the formation of substituted thioureas according to the equation

$$S=C=NR+NHR_2'=CNSHR(NR_2').$$

These reactions proceed with some violence and considerable evolution of heat, but the products, owing to low melting-point and a small tendency to crystallise, remain liquid at room temperature for a long time (whereas the primary thioureas, obtained by the addition of ammonia or primary amines to mustard oils, crystallise excellently).

Examples of the viscosity curves of two such mixtures are given in figs. 54 and 55, in which the extremely marked discontinuity at the maximum and its independence of temperature are clearly shown.

In a more recent paper Kurnakow [25] examines the viscosity

curves of a considerable number of further mixtures, the fusion diagrams of which are to be found in the literature, or have been determined by his collaborators.   The systems
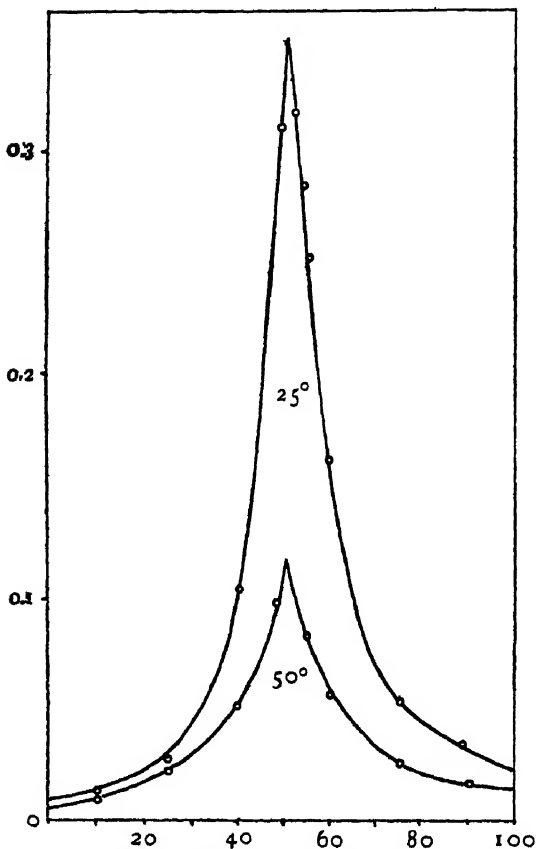
FIG. 54.—Viscosity of mixtures of allyl mustard-oil and methylaniline (Kurnakow). Absc. mols. per cent. of methylaniline. Ord. poises.

naphthalene - nitrobenzene, naphthalene - m-dinitrobenzene, and naphthalene - trinitro - benzene (1: 3: 5) have been shown by Kremann [26] to form solid compounds in equimolar ratios. These compounds do not exist at higher temperatures. Fig. 56 shows the viscosity curve at 90° for the second mixture, which has no maximum in spite of the well-marked discontinuity in the melting-point curve. Further systems studied were mixtures of hydrocarbons with halogen compounds of antimony, and mixtures of hydrocarbons or esters of mono - basic acids with stannic chloride.   The most striking of these is the mixture of ethyl formate with stannic chloride, the viscosity curves of which at 30°, 40° and 50°, as well as the melting-point curve, are shown in fig. 57.   All three viscosity curves have a very sharp maximum (or cusp?) at almost exactly 33 mols. per cent., *i.e.* one molecule of stannic chloride to two of ester; the melting-point also shows a very marked maximum at this ratio. The maximum viscosity is about 71 times that of the more

viscous component, stannic chloride, and about 150 times that of the ester.

A mixture of stannic chloride and acetic acid, investigated
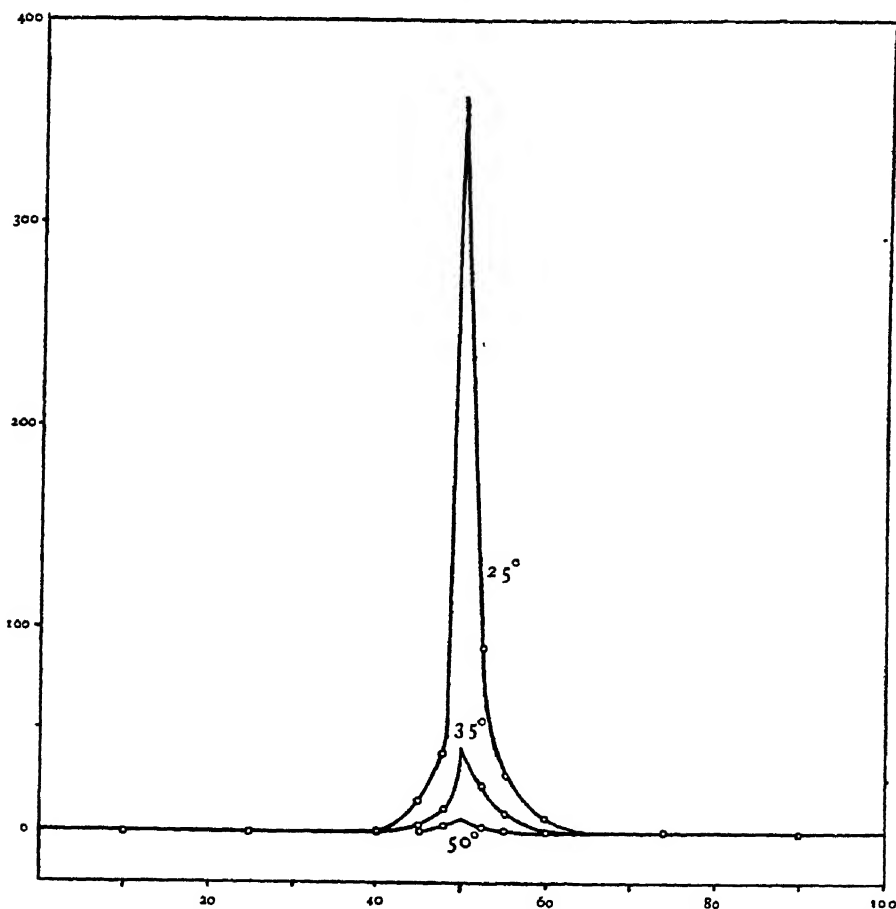
FIG. 55.—Viscosity of mixtures of phenyl mustard-oil and diethylamine (Kurnakow). Absc. mols. per cent. of diethylamine. Ord. poises.

by Stranathan and Strong,[27] shows an even more striking behaviour. The viscosity curve at 25·2° has a sharp maximum, at which the viscosity of the mixture is 263 times that of acetic acid (fig. 58). The maximum is equally marked at 0°, and the viscosity is about 60 times as high as at 25·2°, while its position remains unaltered at the molar ratio 0·25 $SnCl_4$ (fig. 59). There is further evidence of the formation of a

compound of the composition $SnCl_4.3CH_3COOH$, as there is marked evolution of heat on mixing, and a decrease in volume amounting to the very high figure of 32·1 per cent.   Attempts to determine the fusion curve, with a view to confirming the existence of the compound, were made, but proved unsuccessful owing to supercooling and a gradual increase in viscosity, until the mixture became an amorphous solid.

The curves just described appear to have unmistakable maxima rather than the discontinuity postulated by Kurnakow as evidence of compound formation; the decision is a little more difficult with his curves for ethyl formate-stannic chloride (fig. 57), but that for 50° also seems to have a maximum rather than a cusp.
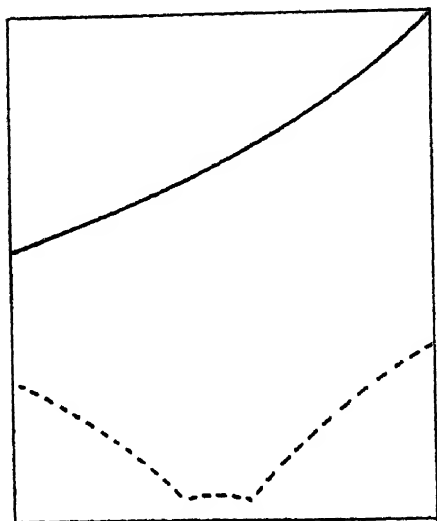
FIG. 56.—Viscosity (full) and melting-point (dotted) of mixtures of naphthalene and m-dinitrobenzene (Kurnakow). Viscosity at 90°.

McLeod's Theory of Mixtures. It is obvious that neither the logarithmic nor the cube-root formula can give a maximum, and no attempt appears to have been made to construct empirical formulæ which will do so.   McLeod,[28] however, has extended the treatment which he applied to pure liquids (*cf.* p. 70) to liquid mixtures with a considerable measure of success, although the complicated nature of the problem compels him to make a greater number of arbitrary assumptions.

McLeod assumes the viscosity of mixtures, like that of pure liquids, to be a function of their free space.   As has been emphasised before, mixtures exhibiting viscosity maxima also show definite contraction; the simultaneous occurrence of both phenomena has been noted by many observers, *e.g.* Dunstan, Thole and Hunt,[29] who, however, do not appear to have assumed a causal nexus between them.   McLeod

takes the view that the increase in viscosity is caused principally by the contraction on mixing, or that, in other words, this contraction has the same effect as contraction by cooling. The considerations which follow apply to liquids having viscosities of the same order only.
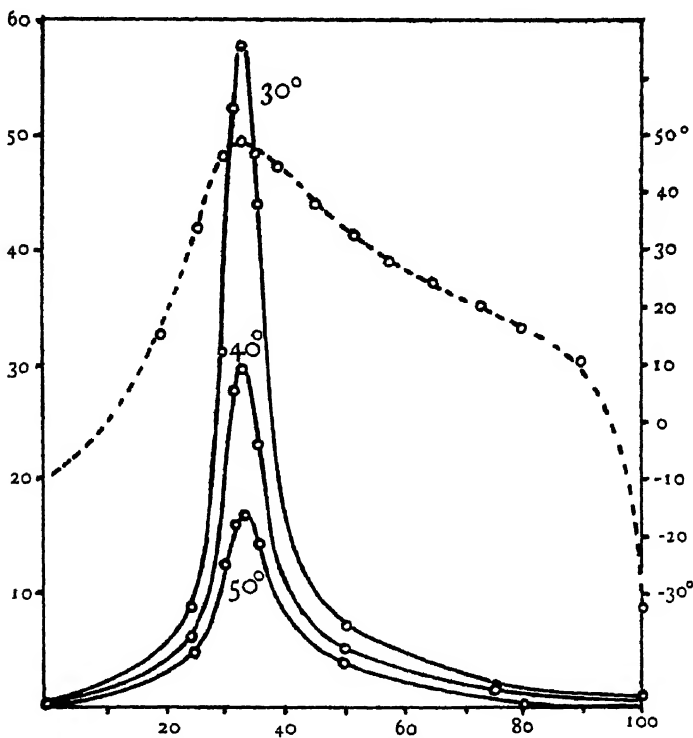
FIG. 57 —Viscosity (full) and melting-point (dotted) of mixtures of ethyl formate and stannic chloride (Kurnakow)   Ord. left, poises , right, temperature.   Absc. mols per cent. of SnCl$_4$.

To arrive at some mathematical expression McLeod proceeds as follows: if two liquids are mixed, one of which has a low viscosity and therefore a large free space, while the other has a high viscosity and a small free space, it seems probable that the liquid with the large free space will share some of it with the more viscous one, whereby the first liquid will have less free space than in the pure state. The less viscous component would therefore contribute more viscosity to the mixture than is proportional to its volume fraction,
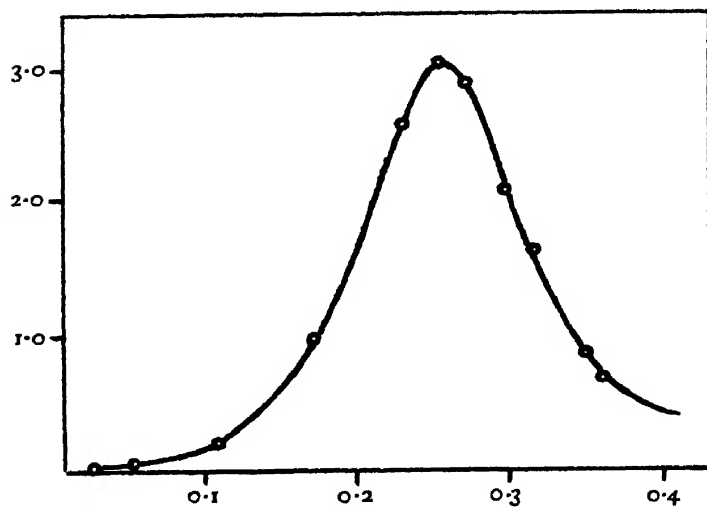
FIG. 58.
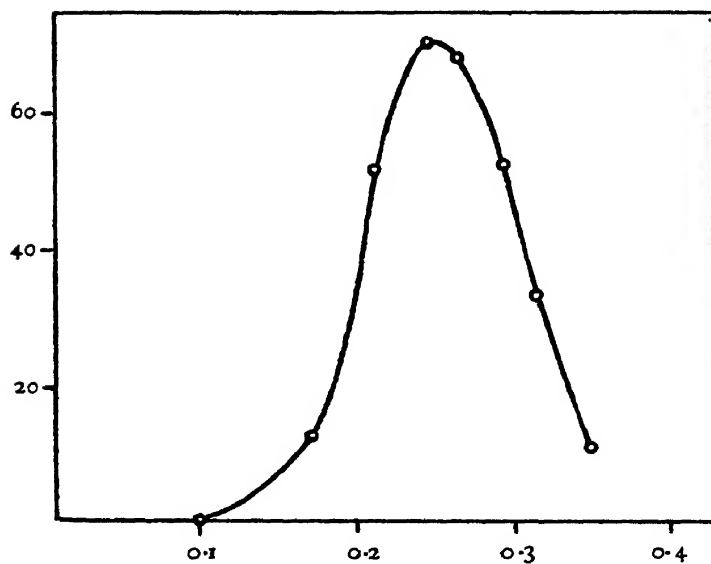
FIG. 59.

Viscosity of mixtures of acetic acid and stannic chloride
(Stranathan and Strong).

FIG. 58.—At 25·2°.   FIG. 59.—At 0°.

Ord. poises.   Absc. molar fraction of stannic chloride.

because its free space has been reduced, while conversely the more viscous component would contribute less on account of a corresponding expansion of its free space.   If we make the simplest assumption, that after mixing the free space is divided between the components in the ratio of their volumes, and assume further that a linear law holds for mixtures of liquids having the same free space, then the true law of viscosity for a mixture of two liquids having initial viscosities η_1 and η_2 ($\eta_1 < \eta_2$), present as volume fractions v_1 and v_2 ($v_1 + v_2 = 1$) with free spaces x_1 and x_2, should have the form:

$$\eta = \eta_1 v_1 \left(\frac{x_1}{x_1 - \Delta x}\right)^{A_1} + \eta_2 v_2 \left(\frac{x_2}{x_2 + \Delta x}\right)^{A_2},$$

where an amount of free space Δx is assumed to be transferred from the less viscous to the more viscous liquid, and A_1 and A_2 are the exponents for the pure liquids (*cf.* p. 70).   As x_1 is assumed $> x_2$, the first term will be increased by a less amount than the second is reduced.   Therefore a mixture of a liquid of low viscosity with one of high viscosity should give a sagged curve, which agrees with experience; in fact, mixing two such liquids would correspond to mixing equal parts of one and the same liquid at different temperatures, when the resulting viscosity is not the mean of the two values, but lies below it.

If x_1 and x_2 are nearly equal, Δx will be small, and the curve very slightly sagged; if there is a considerable contraction on mixing, Δx will be negative in both terms, so that a maximum results; while in the opposite case, *i.e.* expansion on mixing, the viscosity curve will have a minimum.

McLeod states that he has attempted to apply the equation given above to various mixtures exhibiting decided maxima, but that the results, while reproducing the general trend of the experimental curves, were always lower than the observed values.   He assumes a probable explanation of the discrepancy to be that the more viscous component does not gain an amount of free space proportional to its volume— as assumed in the formula—but somewhat less.

Since there is so far no way of determining how the free space is divided between the two components, some further

simplifications become necessary. The linear law is still assumed to hold for mixtures of components with initial viscosities of the same order and without volume change on mixing; in addition, the free space is assumed to be the same in both components, and an arbitrary average value of it is chosen, viz. 0·100. A special difficulty arises when water is the one component, as the free space of water has not been determined accurately.

With these assumptions the formula becomes:

$$\eta = (\eta_1 v_1 + \eta_2 v_2)\left(\frac{0\cdot100}{0\cdot100-C}\right)^{A_1 v_1 + A_2 v_2}$$

where C is the contraction per unit volume. As the assumed free space of 0·100 will be too small for some and too great for other substances, *the values of* A_1 *and* A_2 *will not be those found for the pure substances*, but will have to be calculated from two sets of data for the mixture. C is of course deduced from the density, so that the formula contains two arbitrary constants, the free space being assumed.

McLeod has tested this formula on a number of the mixtures studied by Dunstan, Thole and Hunt,[30] Thorpe and Rodger,[31] and Bramley.[32] The method of calculation is illustrated by Table XXIII. Column 4 gives the volume calculated on the assumption that there is no change on mixing, and column 5 the difference between the calculated and the observed volume of 1 grm. of mixture, divided by the calculated volume, *i.e.* the contraction per unit of original volume. The data for the two ratios marked by asterisks have been used for calculating the exponents, and lead to the values:

A_1 (pyridine) $=4\cdot363$;
A_2 (water) $=5\cdot324$.

TABLE XXIII

Viscosity of Pyridine-Water Mixture Calculated from Contraction (McLeod)

Per cent. pyridine.	Density of mixture.	Volume of 1 grm. of mixture.	Calculated volume.	C/V_c.	η obs.	η calc.
0·00	0·99717	1·00290	1·00290	0·00	0·891	
15·33	1·00119	0·99882	1·00580	0·00694	1·246	1·290
25·55	1·00187	0·99818	1·00719	0·00895	1·4027	1·434
30·99	1·00242	0·99764	1·00882	0·01108	1·6916	1·600
*40·46	1·00359	0·99650	1·01066	0·01401	1·8630	1·863
50·03	1·00365	0·99642	1·01250	0·01588	2·0515	2·040
61·46	1·00282	0·99725	1·01472	0·01722	2·2155	2·157
64·99	1·00295	0·99712	1·01538	0·01799	2·2438	2·237
*75·01	1·0027	0·99972	1·01736	0·01734	2·1151	2·115
79·80	0·99769	1·00235	1·01826	0·01563	1·9201	1·908
87·96	0·99101	1·00925	1·01987	0·01041	1·4424	1·434
94·96	0·98353	1·01683	1·02116	0·00424	1·0801	1·067
100·00	0·97832	1·02217	1·02217	0·00	0·8775	

In fig. 60 the observed values of η are plotted against the percentage composition in full line and crosses, and the calculated values in dotted line and circles. The agreement is remarkably good.

Fig. 61 shows the graph, plotted in the same manner, for the mixture chloroform-ether, where the agreement is again very good. This curve, at the temperature used, has no maximum, nor does the density pass through one. The agreement is less satisfactory for the mixtures ethyl alcohol-water (fig. 62) and acetic acid-water (fig. 63). Regarding the latter, McLeod points out that the discrepancies between the values determined experimentally by different observers are of nearly the same order as those between the observed and calculated values.

McLeod summarises his results as follows: the principal cause of the great increase in viscosity in the mixtures discussed is the contraction which has taken place on mixing, and this contraction is analogous to that produced by cooling.

In support of this view he puts forward the following considerations: the density of a mixture of 90 per cent. of alcohol and 10 per cent. of water at 10° is 0·82654, and $\eta = 2·06$ cp. If there were no contraction on mixing, the density would be
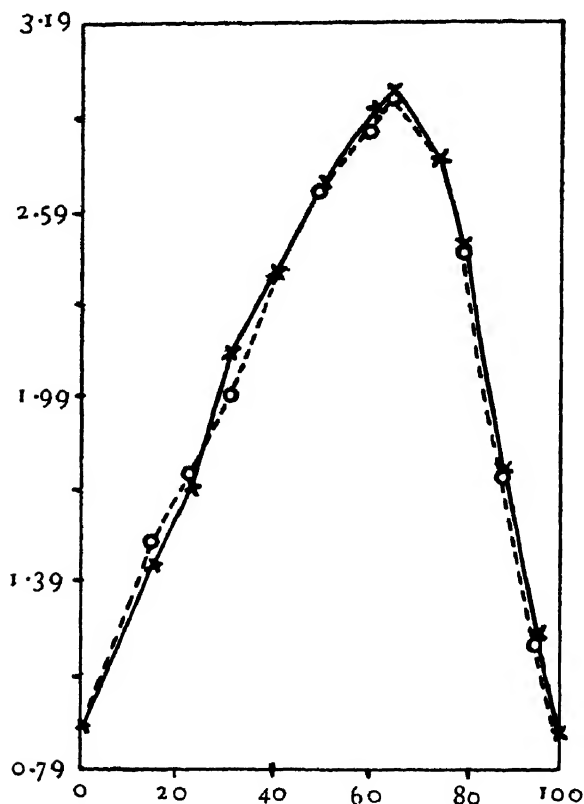
FIG. 60.—Viscosity of mixtures (McLeod). Pyridine-water at 25°. Absc. volume per cent. of first component.

0·81430, and the actual density is reduced to this figure when the temperature is about 24·1°. At this temperature the viscosity of the 90 per cent. mixture is about 1·47, while the viscosity calculated from the linear formula would be 1·44 at 10°. This indicates that the viscosity becomes practically normal when the abnormal density has been overcome by heating.

McLeod has applied the procedure just described to some of the mixtures of organic liquids measured by Bramley;

i.e. he has compared the viscosities at the temperatures required to counteract the contraction with the viscosities calculated for the lower temperature from the linear mixture formula. The agreement is moderate only, but tends to
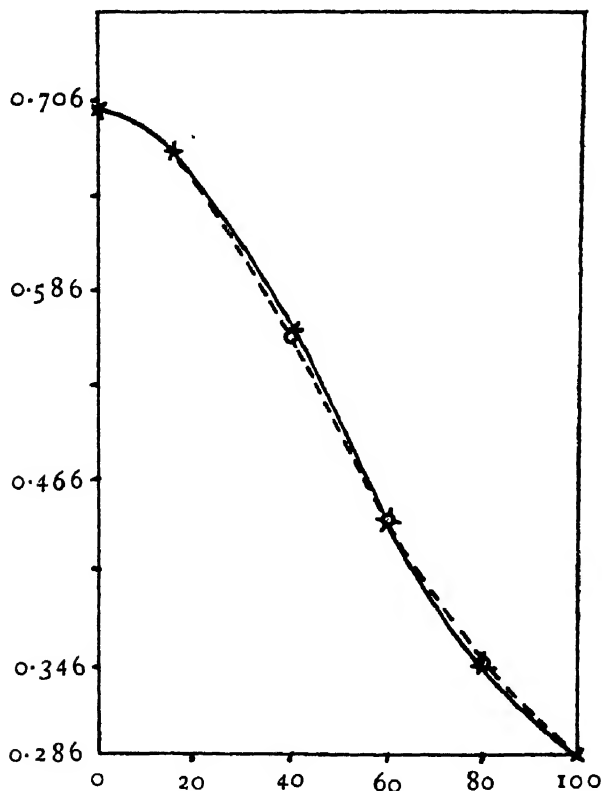
FIG 61 —Viscosity of mixtures (McLeod). Ethyl ether-chloroform at 0°. Absc. volume per cent. of first component.

support the view that the contraction is, at any rate, a very important factor in producing the high viscosity.

The high values of the exponents A, which differ considerably from those for the pure substances (and therefore detract a good deal from the rational character of McLeod's formula) he attributes to association, which enhances the effect of contraction.

In spite of the many difficulties, which McLeod himself recognises, his method of attacking the problem must be

considered the most promising one for the present, and until some theory of the viscosity of pure liquids is available—in the absence of which it is perhaps unreasonable to hope for a solution of the mixture problem. It seems, however,
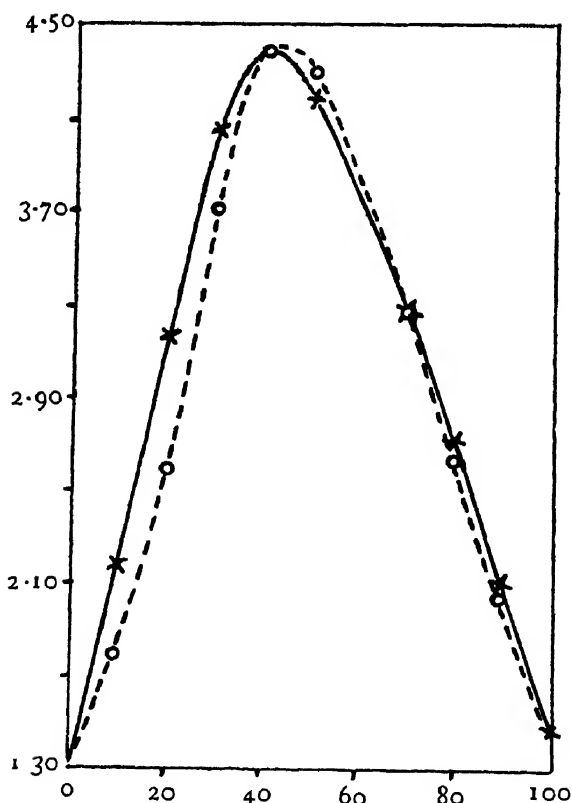
FIG. 62.—Viscosity of mixtures (McLeod). Ethyl alcohol-water at 10°. Absc. volume per cent. of first component.

worth trying whether the method could be improved in one particular: by assuming that the contraction on mixing is equivalent, not to a contraction by cooling, but to a reduction of volume by pressure. Unfortunately, most mixtures have been studied at temperatures lower than 30°, for which Bridgman's data are available. The only example on which a rough test is possible is the alcohol-water mixture, the data for the mixture containing 50·94 per cent. of alcohol by volume at 25° being: η of mixture at 30° $=2 \cdot 02$, η of alcohol

at 30° =1·003, η of water at 30° =0·801, all in centipoises. The actual volume of 1 grm. of the mixture at 30° is 1·0904 c.c., while the calculated volume is 1·13056, so that the contraction per unit volume =0·04016/1·13056=0·0354.   If we
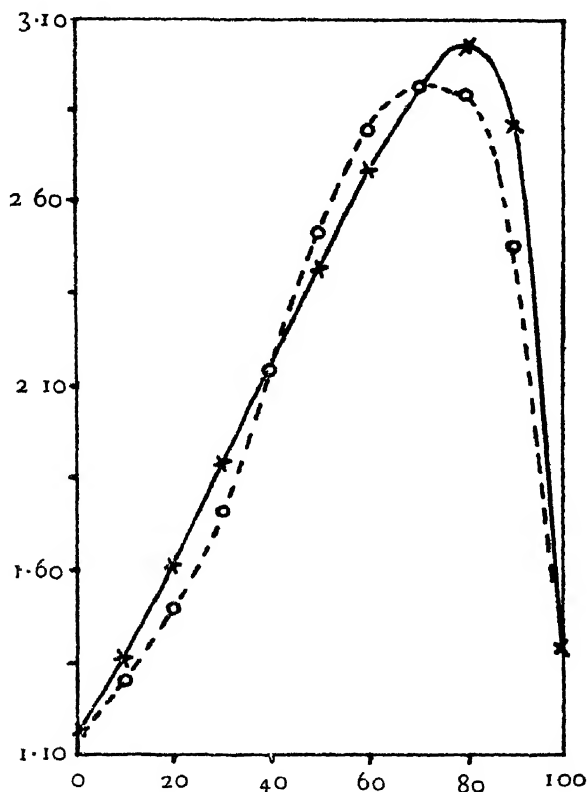
FIG. 63 —Viscosity of mixtures (McLeod)   Acetic acid-water at 15°.   Absc volume per cent. of first component.

assume the compressibility of the mixture to be the mean of that of the components, it is (from Amagat's data for water and alcohol) about 69×10^{-6} per atmosphere, so that the contraction would correspond to a compression of about 500 atmospheres.   Bridgman's figures for the viscosities at this pressure and 30° are: η of water =0·896, η of alcohol =1·5348. The linear mixture formula, with volume ratios, accordingly gives the viscosity of the mixture as =1·235, whereas the actual value, as given above, is 2·02.

The calculation is approximate only, but the discrepancy is so great that it is obviously not possible to treat the contraction caused by mixing as equivalent to compression by external pressure. This method of treatment, of course, also assumes the validity of the linear formula for the compressed mixture, an assumption which, as has been emphasised sufficiently, is not likely to be correct.

It only remains to refer briefly to two types of mixtures: viz. mixtures of two components whose viscosities are very far apart, and solutions of gases in liquids, which—as far as they have been investigated—behave exactly like liquid mixtures.

Mixtures of Components of widely Different Viscosities. The most characteristic of the former is the mixture glycerin-water, the latest data for which, by E. Müller,[33] are given in Table XXIV. The values spread too far to be represented in a graph of reasonable scale, but comparison of the figures at 30° shows the extremely rapid drop in viscosity with increasing water content, the first 17 per cent. of which reduces the viscosity to less than 1/14 of the value for 99·19 glycerin. This large effect of small admixtures of water, and the difficulty of determining them, makes glycerin unsuitable as a standard liquid for calibrating viscometers for viscous liquids.

TABLE XXIV

Viscosity of Glycerin-water Mixtures in Centipoises
(E. Müller)

Tempera-ture.	Weight per cent. of glycerin					
	99·19.	81·98.	61·44.	39·31.	20·29	0.
17°	..	100·7				
18	1393·0	..	..	3·89	2·03	
20	..	72·6	12·27	..	1·90	1·029
30	570·8	40·3	8·57	2·84	1·58	0·817
40	267·5	25·5	5·75	2·11	1·19	0·672
50	175·2	15·1	4·19	1·69	0·97	0·550
60	124·1	12·2	3·23	1·37	0·86	0·455
70	53·3	8·61	2·56	1·16	0·72	0·403
80	32·8	5·68	2·04	1·01	0·64	0·351
90	17·9	5·01	1·69	0·88	0·55	0·317

The viscosity of solutions of gases in liquids has hardly been studied, but Lewis [34] has investigated solutions of sulphur dioxide in carbon tetrachloride, methyl alcohol, benzene, acetone and ether.   Solutions saturated at atmospheric pressure were examined in a viscometer of the Washburn
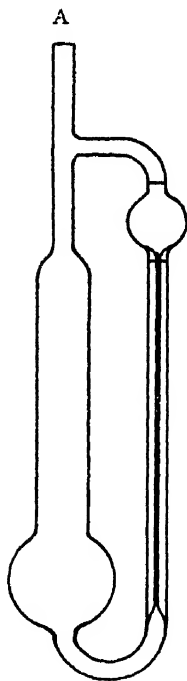
FIG 64 —Lewis's visco-meter for solutions of gases in liquids.
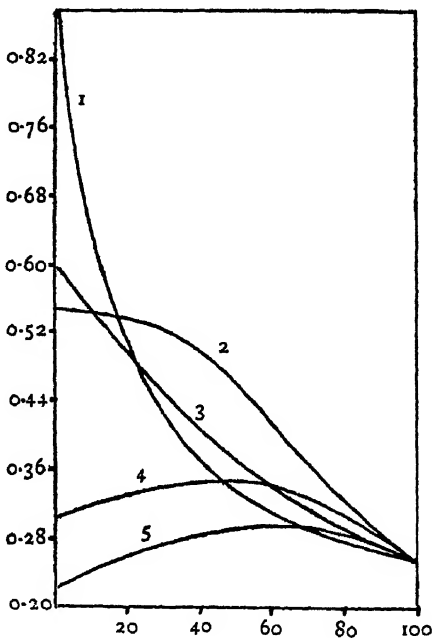
FIG 64A —Viscosity of solutions of sulphur dioxide in organic solvents (Lewis). 1, Carbon tetrachloride , 2, methyl alcohol , 3, benzene , 4, acetone ; 5, ethyl ether

type; solutions containing up to 100 per cent. of SO_2 in the modified Ostwald instrument shown in fig. 64.   The visco-meter was placed in a freezing mixture and filled through A with the solvent and with liquid sulphur dioxide, the contents being determined by weighing.   It was then sealed off at A, placed in the thermostat at 25°, and the small bulb filled by inverting the instrument.   The results are plotted in fig. 64A, and show that the dissolved gas behaves like a liquid; the curves are of the familiar types, except perhaps that for methyl alcohol, which shows a slight inflexion.   The viscosity

of liquid sulphur dioxide at 25° was found to be 0·2550 centi-poise, conforming to the general rule that liquids with high vapour pressures have low viscosities.

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CHAPTER X

VISCOSITY AND CONDUCTIVITY

THE earliest investigations on the viscosity of electrolyte solutions were undertaken by G. Wiedemann [1] with the object of finding a connection between this property and conductivity, and the subject has received a very large amount of attention since then, and more particularly since the theory of electrolytic dissociation began to develop. The assumption that the velocity of ions moving in a viscous medium must be a function of the viscosity is obvious, but equally so is the difficulty of finding a procedure for varying one, and only one, factor at a time. The viscosity of an electrolyte solution can be varied (*a*) by varying the temperature, (*b*) by varying the electrolyte concentration, (*c*) by the addition of a non-electrolyte, and (*d*) by varying the pressure. (*b*) must cause a change in conductivity even if there were none in viscosity, but the converse—that the conductivity is not altered directly—cannot *a priori* be said of any of the three other methods. Change in pressure appears, perhaps, most likely to alter viscosity without directly affecting conductivity much, but owing to experimental difficulties the investigations of this kind are scanty.

Effect of non-Electrolytes. The variation in viscosity and conductivity caused by non-electrolytes and that produced by change of temperature are both easy to study, and both have been the subjects of very numerous investigations. As regards the former, it is interesting that at an early stage attempts were made to obtain an extreme viscosity range by using gelatin as the non-electrolyte—a course adopted by Arrhenius,[2] and soon after by Lüdeking.[3] The complications likely to

be caused by its anomalous viscous behaviour and its effect on the salt concentration were, of course, unsuspected at the time. Arrhenius used 4·2 per cent. of gelatin in zinc sulphate and sodium chloride solution, which set to a jelly at 24°; the conductivity curve between 15° and 32° showed no discontinuity whatever at the setting-point. The conductivity was only about 20 per cent. lower than that of salt solutions of the same concentration without gelatin, and the temperature coefficient of conductivity was practically identical for solutions with and without gelatin. This last result is particularly striking, as the temperature coefficient of viscosity of gelatin sols near the setting-point is many times that of water.

The investigation just mentioned was made in 1885. An explanation which Arrhenius gave about thirty years later will be discussed below. In 1889 Lüdeking again measured the viscosity and conductivity of zinc sulphate solutions containing up to 50 per cent. of gelatin. He found, like Arrhenius, no discontinuity in the temperature-conductivity curves at the setting-point, even with the highest gelatin concentrations. The effect of a given gelatin concentration, however, varied with the salt concentration, or, in other words, the temperature coefficient was no longer independent of the gelatin content, as Arrhenius had found for low gelatin concentrations.

A few years earlier E. Wiedemann [4] had measured the viscosity and conductivity of zinc sulphate solutions in mixtures of water and glycerin; as the latter is a dissociating solvent (*cf.* Getman, p. 128), complications are introduced. He found no proportionality between viscosity and resistance: at the same salt concentration a glycerin-water mixture containing 90 per cent. of the former had a relative viscosity =68·7 and a relative resistance =12·1, the viscosity and resistance of the solution in water alone being taken as unity.

Arrhenius [5] compared the effect of different non-electrolytes in low concentrations, but found that the conductivities at equal viscosities were not the same. A 1 per cent. solution of cane sugar had a relative viscosity =1·046, while 2·2 per

cent. of methyl alcohol was required to give the same viscosity; the conductivity of a given KCl solution was lowered 3·0 per cent. by the sugar and 3·85 per cent. by the alcohol. Arrhenius concludes from this and similar evidence that the reduction of conductivity cannot be a function of the viscosity only.

Heber Green,[6] following the example of Martin and Masson,[7] used sugar as non-electrolyte in an extensive investigation, with lithium chloride as electrolyte. He found that there was no simple proportionality between conductivity and fluidity; when the latter was varied by varying the sugar concentration, the concentration of LiCl remaining constant, the following relation was found to hold approximately:—

$$\Lambda/\phi^n = K.$$

The difference between the extreme values of K amounts to about 8 per cent. of the maximum. Some values of n, deduced by Green from his own and several other observers' results, are given below.

Electrolyte	Non-electrolyte.	n.	Authors.
HCl	Sucrose	0·55	Martin and Masson.
KCl	,,	0·70	
LiCl	,,	0·70	W. H. Green.
CuSO$_4$	Glycerol	1·0	Massoulier.[8]
NaOH	Carbamide	1·0	Fawsitt.[9]
KCl	,,	1·0	

Heber Green makes some observations on the whole problem which deserve to be quoted: " Arrhenius's and Lüdeking's work " (the reference is to solutions containing gelatin (see above)) " indicates that in some cases at least the two fluidities (ionic and physical) are not identical; indeed in such cases they may be compared, on the one hand, to the passage of water through the interstices of a fine sponge, and, on the other, to the sponge itself being forced to flow through the tube in such a way that no circumferential slipping takes place.

" However, we find that several authors are inclined to assume a direct proportionality, and so quote the values

Δ/ϕ or $\dfrac{\Lambda_n}{\Lambda_0} \times \dfrac{\phi_0}{\phi_n}$ as ' ionisation coefficients.'   Thus Bousfield and Lowry,[10] after pointing out that the viscosity of a 50 per cent. sodium hydroxide solution is approximately seventy times that of water, say : ' This increase of viscosity must produce a large effect on the ionic mobility; the influence of this factor may be to some extent eliminated by dividing the molecular conductivity by the fluidity, and this ratio we have called the " intrinsic conductivity " of the solution.' "

In discussing his own results, Heber Green adds: " If we regard each ion as an independent particle threading its way between the molecules of which the solution is composed, then mobility, at any instant, will not depend on the fluidity of the solution, but on the possibility of the ion finding a pore-space through which to pass the section of liquid immediately in front of it, and this, if the dimensions of the ion compared with the pore-spaces are negligible, will be proportional to the 2/3 power of the total free space per unit volume of solution.   If the ionic sizes be larger or the interstitial spaces smaller, then a higher and varying power will be required to express the relation between them."

Although this attempt at a quantitative formulation is somewhat rash, it is hardly possible to disagree with the general view that a system of solvent molecules and solute molecules and ions, to which molecules—of larger, but still comparable, size—of an indifferent substance are added, cannot be looked upon as a continuous medium of which merely the viscosity has been altered by the addition.   In this connection the explanation by Arrhenius of his early experiments on the conductivity of salt solutions, given over thirty years later, is of interest.[11]   After pointing out (*cf.* above) that there is no discontinuity in the conductivity-temperature curve at the setting-point, and that the temperature coefficient in zinc sulphate and sodium chloride solution is practically the same with or without gelatin, he says: " This last circumstance indicates that the colloidal particles of gelatin do not alter, their volume in the temperature interval mentioned above (15° to 32°), and that therefore the setting is not a consequence of increased hydration at falling temperature.   One may

picture this thus: that the gelatin particles form a kind of lattice with very large interstices, and that at the setting temperature they join to form a rigid system, without the interstices being thereby reduced."

Arrhenius therefore assumes that both in the gelatin sol and the gel the ions move through the interstices between the gelatin particles, the only difference between the two being that in the sol the gelatin particles are in motion, whereas in the gel they are joined together. It is difficult to see why ions in a sugar solution should not travel in some similar manner, though what Green calls the " pore-spaces " will be very different in size and number, according as the non-electrolyte is gelatin, with a " molecular weight " of the order 10^4, or cane sugar with a molecular weight of 342.

Attempts to co-ordinate the changes in viscosity and conductivity caused by variation of temperature have also been numerous since Grotrian [12] found the temperature coefficients of both to be approximately the same. Further investigation has shown that the relation is not so simple, but Johnston [13] deduced a parabolic formula for ionic mobility from conductivity measurements by Noyes and his collaborators. This is analogous to Heber Green's formula given above; μ_∞ is the ionic mobility at infinite dilution:

$$\mu_\infty = K\phi^n,$$

where K and n are constants. A number of values of n are given below.

Ion.	K	Na	NH$_4$.	Ag	$\frac{1}{2}$Ba.	$\frac{1}{2}$Ca.	Cl.
n	0·887	0·97	0·891	0·949	0·986	1·008	0·88
μ_∞ at 0°.	40·4	26	40·2	32·9	33	30	41·1

Ion.	NO$_3$.	Acetate.	$\frac{1}{2}$SO$_4$.	$\frac{1}{2}$ Oxalate.
n	0·807	1·008	0·944	0·931
μ_x at 0°	40·4	20·3	42·3	39

The exponent is the greater the smaller the mobility of the ion, or, in other words, the more mobile ions show the greatest deviation from simple proportionality between fluidity and mobility. Both the calcium and the acetate ion have $n > 1$; as it is highly improbable that their speed should increase more

rapidly than the fluidity, there must be a small error, unless the dimensions of these ions are assumed to alter. The results may be summarised as follows: for large ions the change in mobility and in fluidity are proportional to each other, but for smaller ones the speed changes relatively less than the fluidity of the solvent, and the change is the smaller the larger the original speed of the ion.

Temperature Coefficients of Conductivity and Viscosity. The relation between conductivity and fluidity has recently been treated in a new way by M. Wien,[14] who was induced to take up the problem by some observations made by him and J. Malsch.[15] They found that solutions heated by current of very short duration show an " initial temperature coefficient " of conductivity which, for various electrolytes in the same solvent, were practically equal and agreed approximately with the temperature coefficient of the viscosity of the medium. Only when the current was applied for longer periods the value of the temperature coefficient approached that of the " permanent " temperature coefficient, as observed when the liquid is kept continually at the higher temperature. This behaviour suggests the assumption that the effect of temperature change is a combination of two factors: an effect on the viscosity of the solvents which takes place in an imperceptibly short time, and a second effect, specific for the ion, which takes time to manifest itself.

Wien finds that relations become clearest when the temperature coefficients are considered. He defines the temperature coefficient α of fluidity ϕ and the temperature coefficient β of conductivity λ in the region of temperature t as follows:—

$$\alpha = \frac{1}{\phi_t}\frac{d\phi_t}{dt} \qquad \beta = \frac{1}{\lambda_t}\frac{d\lambda_t}{dt} \quad . \qquad . \qquad . \quad (1)$$

The temperature coefficient α of the fluidity of water and aqueous solutions can be represented by the equation

$$\alpha = \frac{1}{a+bt} \quad . \qquad . \qquad . \qquad . \quad (2)$$

By introducing this value for α and integrating, we obtain

$$\phi_t = \phi_\tau [1 + q(t-\tau)]^n \quad . \qquad . \qquad . \quad (3)$$

where $n = \mathrm{I}/b$ and $q = b/a$. The equation has the same form as one of Slotte's formulæ, and gives good agreement with Hosking's experimental data.[16]

The curve for β, the temperature coefficient of conductivity, as a function of temperature, generally runs parallel to the a-t curve, so that in the interval from $0°$ to $100°$ the relation $\beta = a + \gamma$ holds good. With a single exception γ is negative, and for neutral salts approximately -0.2 to -0.3, for bases -0.5 to -0.7, and for acids -0.8 to -1.6. γ is a quantity characteristic of the ion.

In the majority of solutions γ is, within the limits of experimental error, independent of the temperature, and varies little, if at all, with concentration. Larger variations occurring only in solutions of several acids and acid salts are probably caused by changes in the constitution of the ions.

By writing

$$\beta = a + \gamma = \frac{\mathrm{I}}{a + bt} + \gamma \qquad . \qquad . \qquad . \qquad (4)$$

and integrating, the expression for the conductivity is obtained:

$$\lambda_i = \lambda_\tau [\mathrm{I} + q(t - \tau)]^n e^{\gamma(t - \tau)} \qquad . \qquad . \qquad . \qquad (5)$$

in which the factor $[\ ]^n$ represents the variation of fluidity of the solution with temperature, and the exponential factor depends on the nature of the ion.

The negative sign of γ indicates that the conductivity of electrolyte solutions does not increase as rapidly with the temperature as the fluidity. (*Cf.* the exponents found by Johnston above.) In comparing the curves for λ and ϕ it has to be considered that the integration constant, and therefore the origin of the curves, is arbitrary. One may therefore either assume that λ for some reason is greater than would correspond to the fluidity, and that the difference decreases with rising temperature; or that λ is smaller than corresponds to ϕ, and that the difference increases with rising temperature.

In very dilute solutions, when the temperature coefficient of viscosity can, without sensible error, be taken to be the same as that of water, γ can be calculated immediately.

For higher concentrations α deviates markedly from the value for water, and must be determined from direct viscosity measurements. Wien remarks on the lack of adequate data, and takes Hosking's observations on viscosity and conductivity as the most suitable example. Table XXV gives α and β, calculated from the respective measurements, and γ as their difference. For the lithium chloride solution the constancy of γ is satisfactory; for the sodium chloride solution it is so at the higher temperatures, while at the lower ones γ varies irregularly.

TABLE XXV

FACTORS α, β, AND γ IN WIEN'S EQUATIONS

	NaCl, 4N.				LiCl, 2·97N.		
t.	α per cent	β per cent.	γ.	t.	α per cent	β per cent	γ.
10°	2·72	2·36	0·36	10°	2·76	2·54	0·22
20	2·32	2·06	0·26	20	2·34	2·13	0·21
30	2·02	1·87	0·15	30	2·04	1·85	0·19
40	1·79	1·61	0·18	40	1·80	1·62	0·18
50	1·61	1·41	0·20	50	1·62	1·43	0·19
60	1·46	1·23	0·23	60	1·47	1·27	0·20
70	1·34	1·07	0·27	70	1·34	1·13	0·21
80	1·24	0·99	0·25	80	1·24	1·03	0·21
90	1·14	0·87	0·27	90	1·15	0·93	0·22
		Mean	0·25			Mean	0·20

At low concentrations—up to N/10 for one or two electrolytes—the constancy of γ is so marked that Wien feels no doubt of the relation $\alpha + \beta = \gamma$ representing a real property of electrolyte solutions. The physical meaning of γ, an effect which takes time to develop, is not clear, and Wien points out that possible explanations involve difficulties. Both dissociation and hydration may conceivably take time to attain their full values, but to account for the observed facts dissociation would have to decrease and hydration to increase with rising temperature, neither of which assumptions is probable.

An empirical formula identical with equation (5) was used by Bousfield and Lowry,[17] who multiplied Slotte's equation by a " dissociation factor " $e^{-b(t-\tau)}$.

Kraus's Summary. The most complicated case is obviously (b), change of viscosity caused by change in concentration of the electrolyte itself. The problem, as Kraus [18] points out in a summary, the substance of which follows here, arises as soon as the concentration approaches normal, and frequently at lower concentrations. It cannot be assumed *a priori* that the viscosity of the solution is the only factor which influences the velocity of the ions.

The fundamental difficulty in attacking the problem is that the law connecting concentration and conductivity in aqueous solutions of strong electrolytes is not known for concentrations at which the viscosity of the solution is appreciably higher than that of the pure solvent (*cf.* p. 180). Recourse must therefore be had to empirical relations, one of which, found by Kraus and Bray,[19] holds for a large number of electrolytes:

$$(ca)^2/c(1-a) = D(ca)^n + K \qquad . \qquad . \quad (6)$$

where D, n, and K are constants, c the concentration, and a the degree of ionisation, $a = \Lambda/\Lambda_0$, Λ being the conductivity at concentration c, and Λ_0 the equivalent conductivity at infinite dilution.

Kraus considers that the wide range over which this formula applies justifies its use as an extrapolation formula to concentrations at which the viscosity change becomes appreciable, when the influence of this factor can be determined by comparing the observed values with those calculated from the formula.

The use of an empirical equation in this manner is open to considerable objections, as has been pointed out by Rabinovich.[20] Kraus, however, considers that the validity of the procedure can be checked by applying it to a system with " negative viscosity," such as potassium iodide in water. As has been shown above, the viscosity of such a solution passes through a minimum, and eventually becomes equal to that of water; the point at which this happens thus becomes a point of reference at which the observed value should agree

equation, the log-log curve becomes a straight line (fig. 66); uncorrected values give the points marked by crosses.   The maximum difference amounts to about 30 per cent.

Kraus considers that these results prove the applicability of equation (6) to solutions of potassium iodide in water up to 5·66 N, and show that the speed of the ions over this range is a linear function of the fluidity.   The lowering of viscosity produced by this salt at 0° is the largest for which both conductivity and viscosity data were available when he wrote (since when Rabinovich has found that cæsium chloride in high concentrations produces still lower viscosities), but the same method of calculation was applied to solutions of ammonium chloride and potassium chloride at 18° with good agreement.

Kraus further examines the solution of lithium chloride—which increases the viscosity at all concentrations—using
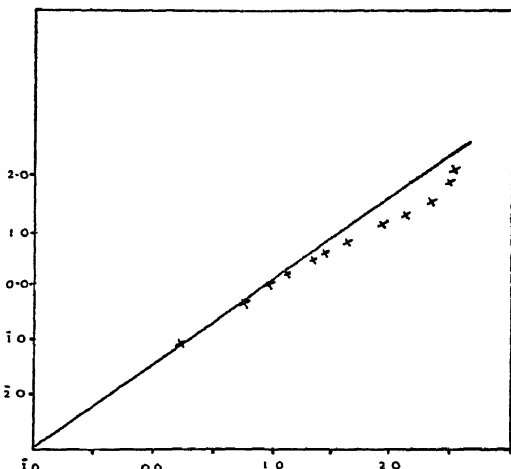
FIG   66.—Log- (corrected   conductivity) log concentration graph of potassium iodide solutions (Kraus)

Washburn and MacInnes's [21] data.   Here the log-log curves defined above are not straight when either the uncorrected values for conductivity or the values corrected by multiplication by η/η_0 are introduced into the equation; a straight line is, however, obtained when the observed values are corrected on the assumption that the speed of the lithium ion varies directly as the fluidity, while the speed of the chlorine ion remains constant.   This method of correction, however, holds only up to normal concentration, beyond which further complications arise.   The grounds on which this discrimination between the two ions is based will be more conveniently stated when a summary of Kraus's views on the effects of pressure has been given.

The only data available for conductivity of salt solutions at high pressures were those of Tammann [22] for N/10 sodium chloride at pressures up to 4000 kg./cm.[2] at 0° and 20°; the viscosity of water has since been determined by Bridgman (*loc. cit.*, p. 82) at 0°, 10·3°, and 30°. In fig. 67 the relative resistances R/R_0 (full lines) at the two temperatures, and the relative viscosities of water (dotted lines) at 0° and 10·3°, are plotted as ordinates against the pressures as abscissæ.
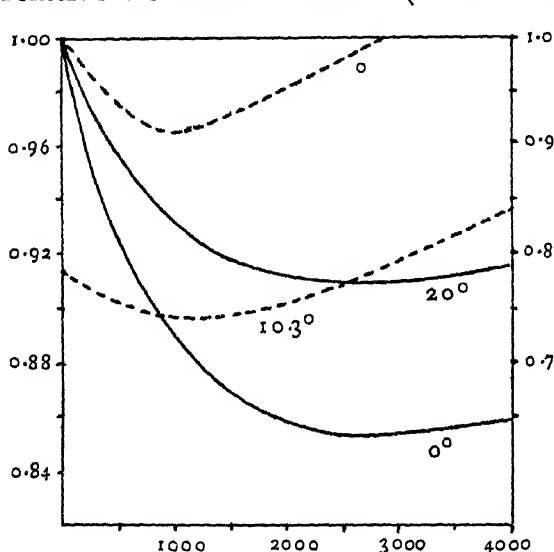
FIG. 67.—Relative resistance (full) of sodium chloride solutions and relative viscosity (dotted) of water. Ord left, R/R_0; right, η/η_0. Absc kg./cm.[2] (Kraus after Tammann).

The viscosity of water, as has already been described, at low temperatures shows a marked minimum at about 1000 kg./cm.[2], which flattens with rising temperature and disappears above 30°. The η-p curves thus bear an obvious resemblance to the η-c curves of solutions of salts which lower the viscosity of water, and Tammann takes the view that there is parallelism between the effect of external pressure and the effect of solutes on the internal pressure. The same kind of change in the molecular constitution of the liquid takes place in both cases, and there is general agreement that the change produced by pressure consists in the breaking up of molecular aggregates.

There is an evident close connection between the R/R_0-p curves and the η-p curves, but Kraus makes no attempt to formulate it quantitatively, and further data on the viscosity change with pressure in salt solutions would be required before this could be done.

If the viscosity at atmospheric pressure is varied by varying the concentration of NaCl, the conductivity change is much smaller than the viscosity change, while the change in conductivity produced by pressure is approximately proportional to the fluidity change. This shows that the effect of viscosity change on the mobility of the same ions differs according to the means by which the viscosity change is brought about.

Kraus next discusses solutions of salts which raise the viscosity of water. They also must be assumed to cause the breaking up of molecular aggregates, but the resulting decrease in viscosity is overbalanced by an increase " due to large ions and non-ionised molecules "; the sum of the effects being that the η-c curve rises more slowly at low concentrations than at higher ones. These considerations explain why the conductivity of solutions with " negative " viscosity can be corrected by multiplying by η/η_0, while this correction is not applicable in solutions with increased viscosity.

Kraus then considers the effect of difference in the size of the ions, and concludes that, when this is sufficiently great, the speed of the smaller ion will " in the limit " not be affected by the change in fluidity, while the speed of the larger ion will vary in proportion to it. The transport number must then be affected, and Kraus finds ample experimental evidence that there is such a change, and that it is in the right direction, i.e. corresponds to a smaller relative speed of the more slowly moving ion. Thus with increasing concentration the transport number of the lithium ion in lithium chloride decreases, while in hydrochloric acid that of the chlorine ion decreases. These conditions account for the possibility, mentioned above, of correcting the conductivities within limits by applying a correction for the lithium ion only.

The conclusion to be drawn from Kraus's survey is that at present there is no method of correcting conductivities for the fluidity change, except in solutions with negative viscosity, where introduction of the values, corrected in direct ratio to the fluidity change, into an empirical equation leads to good agreement with the experimental data. In a recent paper Rabinovich [23] expresses doubts regarding the validity of conclusions drawn from the application of an empirical formula,

and describes an investigation of highly concentrated salt solutions undertaken with the object of testing whether the ordinary correction leads to useful results. The salts used include cæsium chloride, which lowers, and halogen salts of cadmium, which raise the viscosity of water. The general result is that if the ordinary correction is applied, *i.e.* if the observed conductivities are multiplied by η/η_0, the conductivity-concentration curves become anomalous; with increasing concentration the decrease in molecular conductivity becomes slower, reaches a minimum, and then grows again. The simple assumption that the speed of the ions is directly proportional to the fluidity therefore leads to an " over-correction "; the assumption leaves out of account the decrease of ionic diameter caused by decreased hydration. A further discussion on the question whether over-correction alone is sufficient for the anomaly, or whether other causes contribute, is outside the object of this chapter.

Electrolytes in Organic Solvents. The anomalous behaviour of water plays a considerable part in the discussions which have been outlined above, and it is reasonable to expect that the relation between viscosity and conductivity may be simpler in other solvents. Walden [24] has investigated such solutions of tetraethyl ammonium iodide, a strong binary electrolyte with large cation, in a great number of organic liquids. He finds that the conductivity at infinite dilution is directly proportional to the fluidity (varied by varying the temperature), so that

$$(\eta_\infty \Lambda_\infty)_{25} = (\eta_x \Lambda_\infty)_0 = \text{const.}$$

For the electrolyte mentioned, $N(C_2H_5)_4I$, the constant varies between 0·634 and 0·777, with a mean value of 0·700.

Dutoit and Duperthuis [25] tested this relation, using sodium iodide as electrolyte, and several alcohols, acetone and pyridine as solvents. They found that the product $\eta_\infty \Lambda_\infty$ varied with temperature, the variation amounting to +47 per cent. in iso-amyl alcohol, and +25 per cent. in iso-butyl alcohol, when the temperature was raised from 0° to 80°. They also found different values for the product in different solvents, which did not tend to a single value at high tempera-

ture, the extreme values at 0° being in the ratio 100 : 154, and at 80° in the ratio 100 : 215. They conclude that Walden's rule is valid, and that approximately, for a single instance only.

Walden, in reply,[26] criticises the use of sodium iodide as electrolyte, since there is evidence of decomposition, and points out that Dutoit and Duperthuis determined the limiting conductivity by measurements at extremely low concentrations, while he obtained it by Kohlrausch's extrapolation formula, the validity of which for solvents other than water he considers proved by the work of Philip and Courtman.[27] The discrepancies largely disappear when Walden's values for the conductivities are used. Values for the conductivity of potassium iodide in various organic solvents, taken from the literature, also give a constant product. Finally, Walden investigates tetramethyl ammonium iodide in ten organic solvents, and again finds his rule confirmed satisfactorily.

In a more recent paper [28] Walden returns to the subject, and suggests that deviations from the rule may be due to changes in the ionic diameter, *i.e.* the dimensions of the solvent envelope, caused by the changes of temperature. He therefore examines electrolytes consisting on the one hand of simple ions, and on the other of highly complex cations or anions, and finally a salt the anion and cation of which are both complex. He finds that his rule holds excellently for tetra-amyl ammonium iodide, $N(C_5H_{11})_4I$, the cation of which contains 65 atoms, and for triamyl ammonium picrate, $CH_2(NO_2)_3OH.N(C_5H_{11})_3$, the anion of which consists of 18 and the cation of 50 atoms. For the picrate the rule even holds in aqueous solution.

Walden concludes generally that the rule holds the better the larger the ions in comparison with the molecules of the liquid; deviations therefore occur principally in highly associated liquids.

At higher concentrations no simple relation between conductivity and viscosity in organic solvents has yet been found. It is hardly necessary to do more than quote the conclusion reached by Robertson and Acree [29] as the result of a very comprehensive investigation of various electrolytes in ethyl

alcohol. The following remarks refer to sodium iodide: " No method is known at present for . . . correcting the conductivities for viscosity, with certainty. . . . The relations of the viscosities and the conductivities of N/1, N/2 and N/4 solutions of sodium iodide . . . at 25° and 35°, for example, are such that if we were to apply Noyes' method " (*i.e.* multiplying by η/η_0) " we should arrive at the conclusion that the per cent. of ionisation is practically the same for the N/1, N/2 and N/4 solutions of each salt. Such a conclusion is, however, not in harmony with all of the known facts of physical chemistry, and certainly is not borne out by our other experimental results." King and Partington [30] in a very recent paper reach the same conclusion, that correction by multiplying by the viscosity ratio leads to impossible results for solutions of sodium thiocyanate in ethyl alcohol.

Strong Electrolytes. The recent developments in the theory of strong electrolytes, as described authoritatively in the general discussion organised by the Faraday Society (*Trans.*, vol. xxiii, 1927), do not appear yet to have led to any relation between " the mobility of an ion in a solution of appreciable concentration (free from non-electrolytes) and the actual macroscopic viscosity of the solution " (Allmand, *loc. cit.*, p. 349). The reader interested in the subject is referred to this report in general, and in particular to the contributions by Onsager, p. 356; Remy, p. 384; Ulich, pp. 388 and 415; Porter, p. 413; etc.

[1] G. WIEDEMANN, *Pogg. Ann*, **99**, 221 (1856).
[2] S. ARRHENIUS, *Öfvers. d. Stockh. Akad.*, No 6, p 121 (1885)
[3] CH. LÜDEKING, *Wied. Ann.*, **37**, 172 (1889).
[4] E. WIEDEMANN, *ibid.*, **20**, 537 (1883)
[5] S. ARRHENIUS, *Zeit. physik Chem.*, **9**, 487 (1892).
[6] W. H. GREEN, *J. Chem. Soc.*, **93**, 2023 (1908).
[7] C. J. MARTIN and O. MASSON, *ibid.*, **79**, 707 (1901)
[8] MASSOULIER, *C.R.*, **130**, 773 (1900).
[9] E. E. FAWSITT, *Proc. Roy. Soc. Edin.*, **25**, 51 (1903).
[10] W. R. BOUSFIELD and T. M. LOWRY, *Phil. Trans.*, A, **204**, 253 (1905).
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[12] O. GROTRIAN, *Pogg. Ann.*, **157**, 130 (1875); **160**, 238 (1877).
[13] J. JOHNSTON, *J. Amer. Chem. Soc.*, **31**, 1010 (1909)
[14] M. WIEN, *Ann. d. Phys.*, **77**, 560 (1925).

[15] J. MALSCH and M. WIEN, *Physik. Zeitsch.*, **25**, 559 (1924).

[16] R. HOSKING, *Phil. Mag.*, **49**, 274 (1900).

[17] *Loc. cit.* (10).

[18] CHAS. A. KRAUS, *J. Amer. Chem. Soc.*, **36**, 35 (1914).

[19] KRAUS and BRAY, *Trans. Amer. Electrochem. Soc.*, **26**, 143 (1912).

[20] A. J. RABINOVICH, *Zeit. physik. Chem.*, **99**, 338 (1921).

[21] W. E. WASHBURN and D. A. MacINNES, *J. Amer. Chem. Soc.*, **33**, 1686 (1911).

[22] G. TAMMANN, *Wied. Ann.*, **69**, 770 (1899).

[23] *Loc. cit.* (20).

[24] P. WALDEN, *Zeit. physik. Chem.*, **55**, 246 (1906).

[25] P. DUTOIT and H. DUPERTHUIS, *J. Chim. phys.*, **6**, 726 (1908).

[26] P. WALDEN, *Zeit. physik. Chem.*, **78**, 269 (1911).

[27] J. C. PHILIP and H. R. COURTMAN, *J. Chem. Soc.*, **97**, 1261 (1910).

[28] P. WALDEN, *Zeit. anorg. Chem.*, **113**, 85 (1920).

[29] H. C. ROBERTSON and S. F. ACREE, *J. Phys. Chem.*, **19**, 413 (1915).

[30] F. E. KING and J. R. PARTINGTON, *Trans. Faraday Soc.*, **23**, 531 (1927).

agreement with Barus, that it decreased considerably at a pressure of 500 atmospheres.

Reiger [3] studied mixtures of rosin and turpentine, the viscosity of which can be varied within fairly wide limits by varying the ratio of the ingredients. The measurements were carried out by the transpiration method, tubes of 0·3 to I cm. radius and up to 14 cm. long being used. The pressure was generated by a column of mercury kept constant by a simple arrangement. The volumes discharged were, other things being equal, proportional to the pressure within fairly wide limits. A mixture which spread spontaneously in a few days on a plate at 10° showed the following coefficients:—

$$\text{At } 18 \cdot 5° \; \eta = 3 \cdot 01 \times 10^6.$$
$$\text{At } 8 \cdot 6° \; \eta = 67 \cdot 2 \times 10^6.$$

Another mixture, which did not spread appreciably in one month at 10°, was forced through the capillary under a pressure of $1 \cdot 43 \times 10^6$ dynes/cm.² (about 1·5 atmospheres), and showed a coefficient $\eta = 1 \cdot 32 \times 10^9$.

An interesting procedure was adopted to test further whether the flow was in accordance with Poiseuille's Law. The capillary was partly filled with the mixture, which, on cooling, left an approximately flat surface; after pressure had been applied for some time the surface had bulged out. A cast of it was taken, cut in half, the profile projected on a screen, and the ordinates and abscissæ measured by telescope. The profile was found to approximate closely to a parabola, which shows that the flow was in conformity with Poiseuille's Law.

R. Ladenburg [4] examined the same mixture both by the capillary and the falling-sphere method, and obtained results in good agreement when the corrections described on p. 35 had been applied to the measurements made by the second method.

The most complete investigation, as far as temperature range is concerned, and also the most recent, is one by Pochettino [5] on pitch. It is interesting for the further reason that three different methods were used for three temperature

intervals, the results of which fall accurately on one smooth curve.

The first method could be used for the interval from 9° to 50°. The pitch was contained between two vertical coaxial cylinders of radius R_1 and R_2, the length of the tube of pitch being L (fig. 68). The inner cylinder was loaded to the total weight P, and the velocity v_1 with which it descended was measured. It is easy to see that the differential equation for the arrangement is

$$\frac{P}{2\pi r} = -\eta L \frac{dv}{dr}.$$

Integration with the obvious boundary conditions, for $r = R_2$, $v = 0$, and for $r = R_1$, $v = v_1$, gives:

$$\eta = \frac{P}{2\pi L v_1} \log_e \frac{R_2}{R_1}.$$

For the interval from 34° to 80°, which partially overlaps the first, the falling-sphere method was employed. The pitch was enclosed in a thin aluminium tube, and a lead sphere falling through it was observed from time to time by means of X-rays. Finally, above 80°, the capillary-tube method was used.
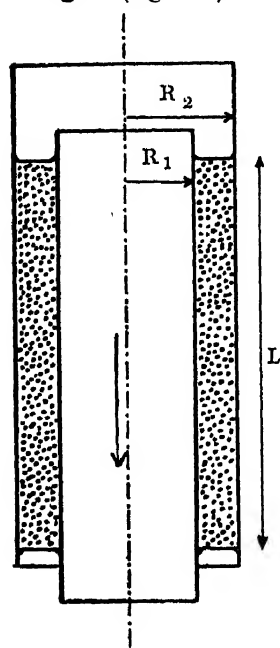
FIG. 68.—Determination of viscosity by axial displacement of concentric cylinders (Pochettino).

The viscosity coefficients found at temperatures between 0° and 99·9° are given in Table XXVI, and the common logarithms of the viscosity are plotted as ordinates against the temperatures as abscissæ in fig. 69. The fact, pointed out already, that the values fall on one curve is specially interesting, as all three methods are based on the assumption that the flow is viscous, and that η is a constant independent of the velocity gradient, so that any deviation from this behaviour would be expected to show itself in view of the very different velocity gradients in the three methods used.

TABLE XXVI

VISCOSITY OF PITCH (POCHETTINO)

Temp.	η (poises).	log η.	Temp.	η (poises).	log η.
9·0	$2\cdot35 \times 10^{10}$	10·371	45·1	$1\cdot64 \times 10^{5}$	5·215
13·3	$5\cdot02 \times 10^{9}$	9·701	50·1	$4\cdot91 \times 10^{4}$	4·691
15·1	$2\cdot57 \times 10^{9}$	9·409	59·0	$1\cdot26 \times 10^{4}$	4·100
17·9	$6\cdot33 \times 10^{8}$	8·801	65·1	$5\cdot77 \times 10^{3}$	3·761
19·0	$4\cdot52 \times 10^{8}$	8·655	70·2	$3\cdot10 \times 10^{3}$	3·491
20·1	$3\cdot30 \times 10^{8}$	8·518	75·4	$1\cdot65 \times 10^{3}$	3·217
25·2	$3\cdot49 \times 10^{7}$	7·543	80·3	$9\cdot23 \times 10^{2}$	2·965
29·8	$7\cdot30 \times 10^{6}$	6·863	86·2	$4\cdot89 \times 10^{2}$	2·689
34·8	$1\cdot75 \times 10^{6}$	6·243	92·8	$2\cdot30 \times 10^{2}$	2·362
39·4	$6\cdot17 \times 10^{5}$	5·790	99·9	$1\cdot19 \times 10^{2}$	2·075

Although the ratio of the viscosities at 9° and 92·8° is 10^8, there is no discontinuity in the log η-t curve. Pochettino
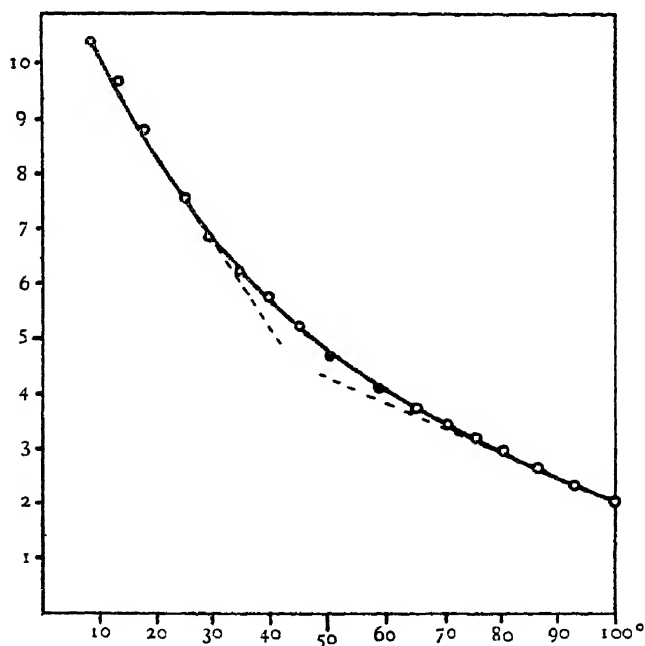
FIG. 69.—Log viscosity-temperature curve of pitch (Pochettino).

points out that the portions between 9° and 32°, and between 75° and 99·9°, are very nearly straight, and refers to an earlier investigation by Heydwiller,[6] who found that this relation, log η_t/t=const., held good for menthol in both the solid and liquid states. Unlike pitch, menthol is a definite substance with a well-defined freezing-point (41·4°), but supercooling down to 34·9° was found possible. There is an enormous discontinuity between the viscosity in the solid and liquid states in the temperature range where both are possible. Heydwiller's results, which make no claim to great accuracy, are:

Solid menthol.	Liquid menthol.
η at 34° $=6\cdot15 \times 10^{10}$	η at 34·9°$=0\cdot2505$
η at 37·2° $=2\cdot41 \times 10^{10}$	η at 37·8°$=0\cdot2036$

poises.

Pochettino suggests that the region between 75° and 99·9° may correspond to the " liquid state," but raises the question what the state of the substance can be assumed to be in the interval between 9° and 32°. Even assuming that the log η-t relation is general, which one set of experiments is hardly sufficient to prove, the comparison is obviously impossible in the absence of any discontinuity.

A point of much greater interest is the absence of breaks in the curve at the points where the method of measurement changes, which—as has been pointed out—seems to prove that the viscosity coefficient is independent of the velocity gradient. Pitch is probably a disperse system, and it is reasonable to expect such anomalies of viscosity as are common in disperse systems, more especially a variation in the apparent viscosity with velocity gradient. That the behaviour of pitch differs from that of an ideally or purely viscous body is proved by some earlier experiments by Trouton and Andrews.[7] These authors measured the viscosity of pitch by clamping cylinders of the material at both ends, one of which was kept fixed, while a constant torque T was applied to the other. The relative angular velocity ω with which two cross-sections (assumed to remain plane) unit distance apart are displaced against each other, as the cylinder is twisted, is a measure of the viscosity,

$$\eta = \frac{2T}{\pi \omega R^4},$$

where R is the radius of the cylinder and η is assumed to be independent of the velocity gradient.   The formula was tested
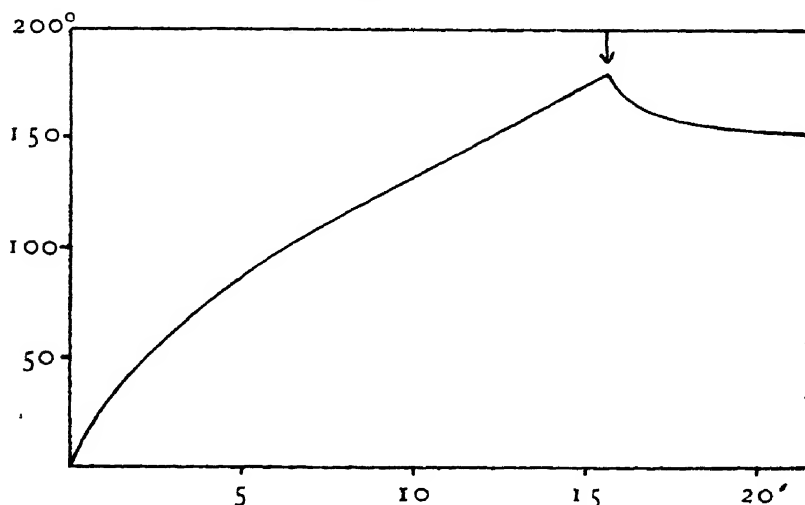
FIG. 70 —Effect of constant torque on pitch cylinder (Trouton and Andrews). Absc. time of application in minutes.   Ord. twist in degrees.

by using cylinders of different radius, when ω was found to be inversely proportional to the fourth power of the radius.
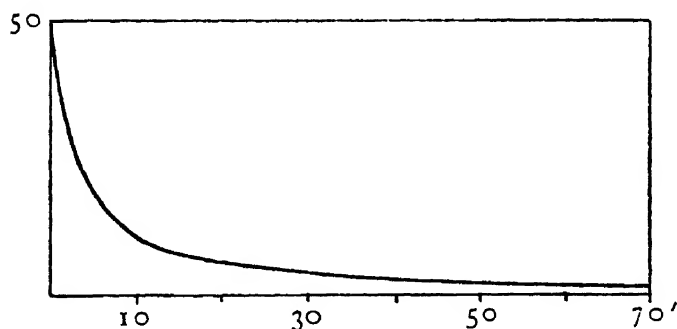
FIG 71 —Relaxation curve of twisted pitch cylinder (Trouton and Andrews).   Absc. time in minutes.   Ord. remaining torque

Elastic Effects.   Tests at constant temperature reveal two departures from simple viscous deformation with constant η, as shown by the two graphs, figs. 70 and 71.   The first

of these shows the increase in twist (ordinates) with time (abscissæ), when a constant torque is applied to the specimen: the twist during the initial period increases more rapidly than the time, a steady state being eventually reached. At the point marked with an arrow the total torque was removed, whereupon the cylinder did not remain stationary but turned backwards, *i.e.* energy in the form of elastic strain was stored in it. The rate of dissipation of this energy, or the relaxa-
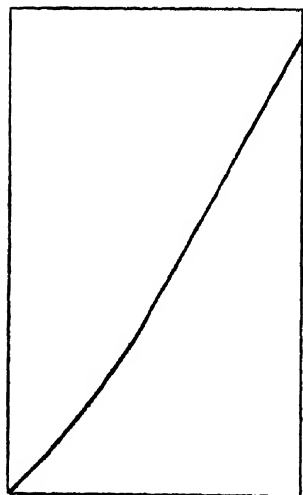
FIG. 72 —Velocity of twist-ing (ord) of pitch cylinder as function of applied torque (absc.) (Trouton and Andrews).

tion, can be measured by reducing the torque at intervals, so that no un-twisting takes place, and plotting remaining torque against time, which graph is shown in fig. 71. The authors point out that the relaxation curve is not, as might have been expected, logarithmic, but that the lower portion can be well represented by a rectangular hyperbola.

Fig. 72 finally shows the relation between applied torque (abscissæ) and velocity of twisting (ordinates) in degrees per minute. The velocity at first increases more slowly than the torque, but above a certain torque becomes proportional to it. The authors suggest as the cause of the anomalous behaviour that, during the first stage of deformation (while it increases more rapidly than the time of application of a constant torque), " a store of elastic energy is gradually accumulated, which is preserved intact during the state of steady rotation, and is given out on removal of the stress to produce the return flow."

The interest of this investigation, when correlated with present knowledge, lies in the fact that a large number of colloidal solutions have been proved to behave in a manner which is closely parallel to that just described. The anomaly is not bound up with a particular range of viscosity values; while Trouton found for pitch at $0°$ $\eta = 5 \cdot 1 \times 10^{11}$ poises, the apparent viscosity of many colloidal solutions exhibiting

anomalies is of the order of centipoises when determined by ordinary methods.

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[2] C. Barus, *Phil. Mag* (5), **29**, 337 (1890) ; *Sillim. J.* (3), **45**, 87 (1893).

[3] R. Reiger, *Drude's Ann.*, **19**, 985 (1906).

[4] R. Ladenburg, *Ann. d. Phys.*, **22**, 287 (1907).

[5] A. Pochettino, *Nuovo Cimento*, **8**, 77 (1914).

[6] A. Heydwiller, *Wied. Ann*, **63**, 56 (1897).

[7] F. T. Trouton and E. S. Andrews, *Proc. Phys Soc. Lond.*, **19**, 47 (1909).

CHAPTER XII

THE VISCOSITY OF COLLOIDAL SOLUTIONS

EXPERIENCE accumulated at an increasing rate during the last twenty years goes to show that the simple relations deduced in Chapter II for the flow through a capillary, and for the moment in the concentric cylinder apparatus, do not hold for a large number of colloidal solutions or even for coarser disperse systems, such as suspensions of microscopic particles. Other things being equal, the volume discharged in unit time through a capillary is not simply proportional to the pressure, but increases more rapidly than the pressure. Similarly, the moment in the concentric cylinder apparatus is not simply proportional to the angular velocity of the outer cylinder, but increases less rapidly than this velocity. This effect would be produced if the viscosity coefficient were not, as in normal liquids, a constant, but were to decrease with increasing pressure in the capillary, or with increasing angular velocity in the concentric cylinder apparatus. The variable obviously common to both methods of measurement is the velocity gradient, which increases with increasing pressure in the capillary and with increasing angular velocity in the cylinder apparatus; so that the anomaly of disperse systems may be stated, at least formally, by saying that the viscosity coefficient is a function of the velocity gradient, of which so far nothing is known beyond the experimental fact that the coefficient always decreases with increasing velocity gradient. Whether a property of this kind is a viscosity, or what else it should be called, are questions which will be fully discussed later on; in the first instance it will be necessary to inquire what a large mass of experimental

material, determined and calculated by the methods applicable to normal liquids, really means.

Measurements have been made by determining the quantities Q_1, Q_2, . . . Q_n discharged from a given capillary at the pressures P_1, P_2, . . . P_n, and from these data the viscosity coefficients η_1, η_2, . . . η_n have been calculated by Poiseuille's formula. Or the deflections θ_1, θ_2, . . . θ_n at the angular velocities ω_1, ω_2, . . . ω_n have been measured, and a number of viscosity coefficients calculated from the formula $\eta = \theta / K \omega$.

Now the equations for the two forms of apparatus have been deduced on the assumption that η is a constant. If, however, it is a function of dv/dr or $rd\omega/dr$, it is obvious that the differential equations must be different from those which hold for normal liquids. The method outlined above therefore amounts to calculating a number of " fictitious " viscosity coefficients ; in other words, the η *of normal liquids which would produce the quantities* Q (*or the deflections* θ) *at the pressures* P (*or the angular velocities* ω) *employed, in an apparatus of the particular dimensions used.* The large experimental material therefore has a qualitative significance only, a limitation to be remembered in considering it. It is also necessary to add that dilute sols of the suspensoid or lyophobe type, and emulsoid or lyophilic sols at temperatures of 40° and over, show no anomalies exceeding the probable experimental error.[1]

Viscosity measurements on colloidal solutions were first carried out by Thomas Graham.[2] When investigating silicic acid sols he discovered one of the fundamental properties of gelating sols, the continuous increase in viscosity with age. " The ultimate pectisation of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid-transpiration tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscosity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinising, silicic acid flows like an oil."

Viscosity measurements—generally by means of the Ostwald

viscometer—subsequently became one of the most widely used methods of investigating colloidal solutions, and much of the material thus accumulated is difficult to interpret. In many of the investigations dealing, *e.g.*, with the changes in viscosity caused by the addition of electrolytes, the results have had to be explained by ancillary or *ad hoc* hypotheses, which often do not admit of independent verification; the vast amount of work on protein sols is a very striking example of this kind. Many researches have been undertaken for technical ends, in the hope of connecting—though only empirically— an easily measured property like viscosity with technically important properties less easy to measure or even to define, like the " nerve " of india rubber, the " strength " of flour, or the adhesive properties of glue. Nevertheless, a few generalisations are possible which hold good independently of the particular chemical nature of the disperse phase.

General Characteristics. The viscosity of stable suspensoid or lyophobic sols is a function of their concentration only and independent of their age or previous history. In many of these sols, however, the concentration is so low that the difference in viscosity between the sol and the dispersion medium is of the same order as the experimental error. Small changes in viscosity with age, such as have been noted in a few instances,[3] may fairly confidently be ascribed to incipient coagulation or changes in the dispersion medium itself.

In sols which admit of higher concentrations, but are of more doubtfully suspensoid character, such as glycogen [4] or sulphur [5] sols, the viscosity increases with concentration at a rate comparable with that of true solutions of non-electrolytes, *e.g.* of cane sugar.

The temperature coefficient of viscosity in suspensoid sols is—again within the limits of experimental error—merely that of the dispersion medium. A convenient way of examining the variation of the temperature coefficient is the following: if η_t and η_t' are respectively the viscosities of the dispersion medium and of the sol at the temperature t, then η_t'/η_t plotted against t will lie on a straight line parallel to the axis of t if the temperature coefficients of sol and dispersion medium are the same. Fig. 73 shows this graph for one

of Oden's [6] sulphur sols with a concentration of 7·68 per cent. The viscosity of the sol decreases somewhat less rapidly than that of water, so that η_t'/η_t increases with rising temperature. Both the sense and the magnitude of the variation differ strikingly from that observed with emulsoid sols.

FIG. 73.—Relative viscosity-temperature curve of sulphur sol (Oden).

In the latter the temperature coefficient is always markedly greater than that of the dispersion medium. Fig. 74 shows the values of η_t'/η_t for a 9·39 per cent. casein (more correctly sodium caseinogenate) sol (Chick and Martin [7]). The shape of the curve indicates that the viscosity of the sol decreases
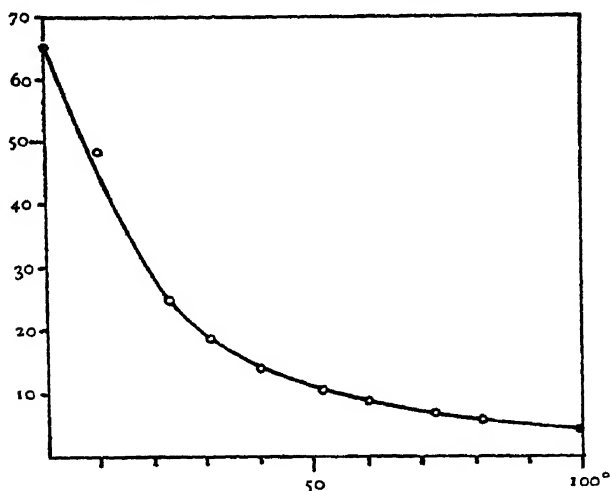
FIG. 74.—Relative viscosity-temperature curve of casein sol (Chick and Martin).

much more rapidly with rising temperature than that of water.

The casein sol does not gelate at low temperature; the sols which do so have still higher temperature coefficients, especially in the vicinity of the gelation temperature.

Another and even more marked characteristic of the

lyophilic sols is the rapid increase of viscosity with concentration even at ordinary temperature, and in sols which do not
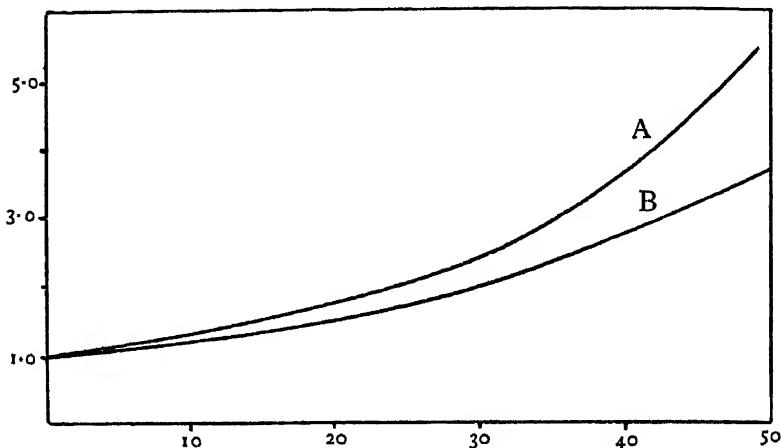
FIG. 75.—Relative viscosity-concentration curves of sulphur sol (Oden). A, amicroscopic ; B, submicroscopic particles.   Absc. grm. in 100 c.c. of sol.
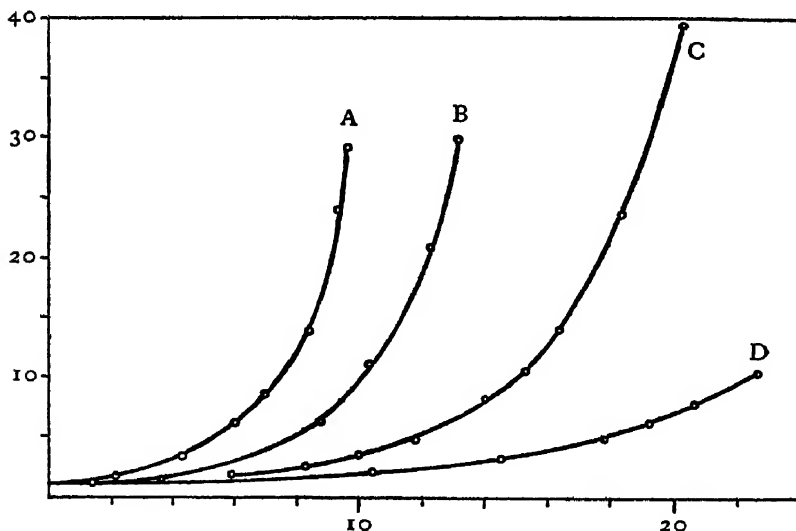
FIG. 77.—Relative viscosity-concentration curves of various protein sols (Chick).   A, sodium caseinogenate ; B, euglobulin (with NaCl) ; C, Pseudoglobulin ; D, serum albumin.   Absc. per cent by weight.

set to gels.   The high viscosity produced by small concentrations is particularly striking in sols with organic solvents,
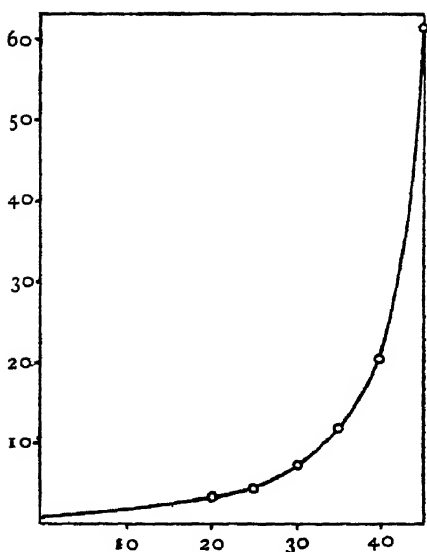
FIG. 76.—Relative viscosity-concentration curve of glycogen sol (Bottazzi and d'Errico). Absc. grm. in 100 c.c. of sol.

where the viscosity at 1 per cent. may be sixty (rubber in benzene) to one thousand (blasting soluble nitrocellulose in acetone) times that of the solvent.

Effect of Concentration in Various Types of Sols. The graphs, figs. 75 to 78, illustrate the variation of relative viscosity (that of the dispersion medium being taken as unity) with concentration in two lyophobe sols, sulphur and glycogen, and a number of lyophilic sols. The relative viscosities have all been calculated by Poiseuille's formula, and, since especially the lyophilic sols all exhibit the anomaly described at the beginning of this chapter, the data are subject to the qualifications made there.

Graham's observation that the viscosity of silicic acid sols increased steadily until gelation occurred has already been mentioned. This increase of viscosity is a characteristic property of all sols which set to jellies, but shows itself even when the concentrations are too low, or, in some instances,

FIG. 78.—Viscosity-concentration curve of cellulose nitrate sol in acetone (Baker). Absc. grm. in 100 c.c. of sol. Ord. centipoises.

the temperatures too high, for the transformation to become complete. Fig. 79 shows relative viscosity of gelatin sols plotted against time,[8] while fig. 80 gives the same data for sols of cellulose acetate in benzyl alcohol.[9]

The Concentration Function. The first attempt to treat mathematically the viscosity of a disperse system is due to Einstein,[10] who considered a suspension of rigid spheres in a viscous liquid. On the assumption that the aggregate volume of spheres was small compared with that of the liquid, and
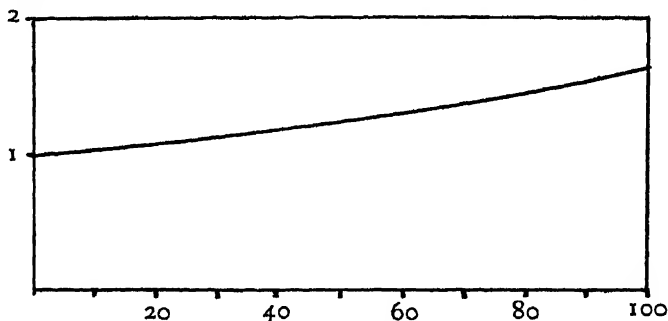
FIG. 79.—Increase in relative viscosity of gelatin sol at 25° with time (mins.) (Levites).

that the spheres were sufficiently far apart not to influence one another, he arrived at the following equation:—

$$\eta_s = \eta(1 + 2 \cdot 5\phi) \qquad . \qquad . \qquad . \qquad (1)$$

where η_s is the viscosity of the suspension, η that of the dispersion medium, and ϕ the aggregate volume of spheres in unit volume of suspension. In 1920 Einstein, in a short communication to the *Kolloid-Zeitschrift*, emphasised that this result was deduced strictly from the fundamental equations of hydrodynamics.

The most striking feature of Einstein's formula is that the radius of the spheres does not appear in it, but only their aggregate volume, *i.e.* the concentration; the viscosity grows in linear ratio with this concentration, provided the system conforms to the assumptions made in deducing the formula.

Before discussing the various attempts to verify the equation, it may be advisable to state here that, ten years after its publication, it was shown by Humphrey and Hatschek [11]

that the viscosity of suspensions of low concentrations (2 to 8 per cent.) was anomalous, *i.e.* varied with the velocity gradient. It is therefore again doubtful how the results obtained by using Poiseuille's formula can be interpreted.
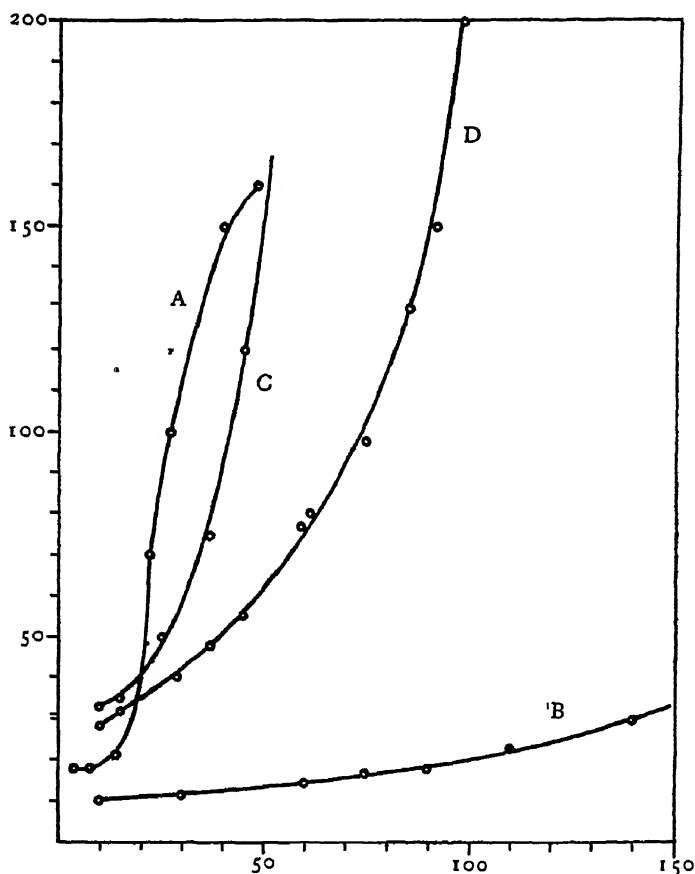
Fig. 80.—Increase in viscosity of cellulose acetate-benzyl alcohol sols with time (Mardles). A, 3 per cent sol at 13·5°; B, the same at 18°; C, 10 per cent sol at 23°; D, the same at 23·5°. Absc. minutes. Ord. times of flow in seconds.

A fundamental difficulty in verifying the formula for suspensoid sols is that it contains the *volume* of disperse phase, whereas, generally speaking, the weight only is known. Even if the density of the particles is the same as that of the material in bulk, as is probable for, *e.g.*, gold sols, the particles do not consist of the pure substance. Silver sols prepared by

Carey Lea's method, which can be obtained in comparatively high concentrations, have particles containing notable amounts of impurities. It is also highly probable that in most sols the particles carry with them layers of liquid which increase their effective volume. Einstein himself applied his formula to a dilute cane-sugar solution, and found it necessary to assume hydration of the sugar molecules to obtain agreement with experimental data.

The first experimental verification of Einstein's formula was undertaken by Bancelin,[12] who determined in the Ostwald viscometer the viscosity of suspensions of gamboge, made by Perrin's method, and containing globules of 0·3, 1·0, 2·0, and 4·0μ radius. As required by the formula, the radius of the particles had no influence. The viscosity was a linear function of the concentration, with a proportionality factor of 2·9 instead of 2·5, as shown by the following table, which gives the results for particles 0·3μ radius at 20° C. (water at 20° = 1) :—

φ (per cent.).	η_s.
0·00	1·000
0·09	1·002
0·24	1·0069
0·33	1·0088
0·53	1·0128
0·66	1·0167
1·05	1·0276
2·11	1·0570

Within these limits of concentration the formula holds good as far as the linear increase in viscosity with concentration is concerned. A more extensive range was investigated by Oden,[13] who determined the viscosity of sulphur sols prepared by Raffo's method, which can be obtained in high concentrations; it is, however, doubtful whether the sulphur particles can be considered as rigid spheres. Oden examined two sols, one with particles, whose diameter was estimated by the usual ultra-microscopic method at 100$\mu\mu$, while the other sol was amicroscopic with particles probably about 10$\mu\mu$ diameter. Fig. 75 shows the results up to a concentra-

tion of 50 per cent.   The increase of η_s at low concentrations is almost linear, but becomes markedly more rapid above about 10 per cent.   The curve for the sol with smaller particles lies entirely above that for the coarser grained, the ratio of the ordinates being approximately constant.   The viscosity is therefore not independent of the particle size, but a given aggregate volume of small particles produces a greater increase in viscosity than the same volume of large particles.

It has been pointed out by Hatschek [14] that the effect of the radius is easily explained if the particles are surrounded by adsorption layers which increase the effective volume.   If the thickness of these layers is assumed to be the same for both sizes, the increase in effective volume will be proportional to the aggregate surface, and therefore greater for the sol with small particles.   The thickness calculated from Oden's data is $0.87\mu\mu$, an entirely probable value which, however, cannot be checked in the absence of a third set of measurements.   It must also be added that in sols of high concentration the fundamental assumption made in deducing Einstein's equation, that the particles do not influence one another, is not likely to hold good.

A further complication arises from the electric charges present on particles, at least in most aqueous sols and suspensions, which Einstein's deduction does not take into account. That such charges must increase the viscosity had been suggested already by Wo. Ostwald; [15]   the mathematical theory for a system of charged spheres in a liquid was developed by Smoluchowski, [16] who deduced the modified Einstein equation

$$\eta_s = \eta\left\{ 1 + 2.5\phi\left[1 + \frac{D\zeta^2}{2\pi\lambda\eta r^2} \right]\right\}$$

in which the new symbols mean:

λ the specific conductivity per c.c. of the liquid ;
r the radius of the particles ;
ζ the potential difference in the double layer ;
D the dielectric constant of the liquid.

It will be noticed that the radius of the particle appears in

this formula, and that the term in square brackets increases with decreasing radius; *i.e.* the viscosity, other things being equal, increases in the same sense. The formula has been verified experimentally by Kruyt and his pupils [17] on a number of sols.

Hess [18] has attempted to deduce synthetically an equation for the viscosity of a suspension. By assuming a simple arrangement of the particles in a liquid flowing through a capillary he arrives at the equation

$$\eta_s = \frac{\eta}{1 - a\phi} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

in which the symbols have the same meaning as before, and *a* is a numerical factor > 1. He calculated *a* from a series of measurements on suspensions of red-blood corpuscles—which, on account of their peculiar shape and easy deformability, are not very suitable for testing a formula to be applied to suspensions—and found that *a* varied from about 2·25 at low concentration ($\phi = 0·10$) to about 1·15 at high concentration ($\phi = 0·79$). It is highly probable that the factor *a* also varies with the velocity gradient.

The theoretical treatment of emulsoid or lyophilic sols presents even greater difficulties than that of suspensions, since some working hypothesis is necessary at the outset to account for the enormous increase in viscosity produced by small concentrations by weight of dispersed material. The assumptions usually made are of two kinds. One is that the molecules or particles of the disperse phase arrange themselves in long threads or " ramifying aggregates " (McBain [19]), so that eventually there is a continuous network of disperse phase. No mathematical treatment of such systems has so far been attempted. The other assumption is that the particles of disperse phase are heavily hydrated (or solvated), so that they occupy a large multiple of the volume calculated from the weight concentration and density. A necessary corollary is that these solvated aggregates are, if not liquid, at least easily deformable, as otherwise the whole system could no longer behave like a liquid.

Hydration has, for instance, been assumed by Arrhenius,[20]

who applied his empirical logarithmic formula to a series of viscosity determinations on protein sols carried out by Harriette Chick and collaborators.[21]   The formula for this purpose was given the form:

$$\log \eta = \theta \frac{100p}{[100 - (n+1)p]} \qquad . \qquad . \qquad (4)$$

in which p is the weight of dry substance dispersed in 100 grms. of sol, θ a constant, and n the hydration factor, $i.e.$ the number of grammes of water associated with 1 grm. of dry weight of disperse phase and thus withdrawn from the free dispersion medium.

The values of θ and n calculated from the experimental data show remarkable constancy, except in one or two instances at the lowest concentrations, and the formula expresses the viscosity of various protein sols with great accuracy. Arrhenius remarks on the fact that the hydration factor is practically constant, while in true solutions hydration always decreases with increasing concentration.   As the reason of this difference he suggests that the vapour pressure of true solutions is lowered considerably with increasing concentration of solute, while the lowering is imperceptible in colloidal solutions.

The logarithmic formula fails when applied to sols of high viscosity in organic solvents, such as the cellulose nitrate sols investigated by Baker,[22] or the cellulose acetate sols studied by Mardles.[23]   The solvation factor becomes irregular and occasionally negative.[24]   Baker himself succeeded in representing his results with fair accuracy by a parabolic formula:

$$\eta = \eta_0 (1 + ac)^n,$$

in which η_0 is the viscosity of the solvent, a and n are constants, and c the concentration in grm. per 100 c.c. of sol.

Hatschek has treated the problem of a dispersion of liquid, or elastically deformable, particles aggregating more than about one-half of the total volume by a geometrical method.[25] When such a system is sheared the particles undergo deformation, and, at low velocity gradients, recover their shape owing to interfacial tension or elasticity.   When, however, a certain

velocity gradient is exceeded they are ·assumed to remain
deformed throughout. During the first regime the viscosity
of the system must vary with the velocity gradient; during
the second it is constant, and given by

$$\eta_s = \frac{\eta}{1 - \sqrt[3]{\phi}} \qquad . \qquad . \qquad . \qquad (5)$$

where the symbols have the same meaning as before, and ϕ
is assumed to be > 0.5.

The formula has hardly been tested for emulsions, which
are systems conforming to the assumptions made in deducing
it. It does not contain the viscosity coefficient of the dis-
perse phase, which would be expected to play some part in
determining the viscosity of the system. The formula, how-
ever, represents fairly accurately the viscosity of suspensions
of red-blood corpuscles—which are easily deformable—as was
first shown by Trevan,[26] whose data are given below. The
first column gives the viscosity of the suspension (determined
in an Ostwald viscometer), the second ϕ determined in the
usual way (centrifuging in graduated tubes), and the third
ϕ calculated from

$$\phi = \frac{(\eta_s - \eta)^3}{\eta_s} \qquad . \qquad . \qquad . \qquad (6)$$

η_s.	φ (Measured).	φ (Calculated).
4·42	0·470	0·462
4·96	0·515	0·500
4·97	0·521	0·510
6·01	0·583	0·580
6·53	0·593	0·608
7·10	0·625	0·635
11·13	0·735	0·745
15·05	0·791	0·789
30·50	0·905	0·910

The values of η_s are relative, η being taken $= 1$. The measured
and calculated values of the concentration agree within ± 1
per cent., which is the order of the experimental error in
determining the volume. The formula gives equally good

agreement when applied to Hess's viscosity determinations (*cf.* p. 200).

The application of the formula to lyophilic sols presents a fundamental difficulty, even if the assumption that these sols contain separate liquid or elastically deformable particles is granted. These particles are assumed to consist of the dispersed substance plus some dispersion medium—associated with it by some mechanism at present unexplained—which increases the volume of disperse phase and reduces that of dispersion medium.

Hydration. A " hydration factor " can be calculated from the observed viscosities and from the known *weight concentration* ϕ':

$$h\phi' = \frac{(\eta_s - 1)^3}{\eta_s} \qquad . \qquad . \qquad . \qquad (7)$$

h is the factor by which the weight concentration must be multiplied to give the volume concentration which enters into the formula.

If this calculation is applied to typical emulsoid sols, *e.g.* of proteins, the constancy of h is reasonable over a moderate range of concentration. The absolute value, *e.g.* 8 to 9 times the weight of dry substance for sodium caseinate, has been pronounced highly improbable by Arrhenius, who finds hydration factors of 2 or less for various proteins.

The question which values are more probable cannot be settled until some independent method of measuring hydration or solvation is found, of which there is at present no prospect. There are, however, considerations which make factors much higher even than 9 seem by no means unlikely. A large number of colloids swell in the solvent before dispersing, and it is reasonable to assume that this association persists in the particles into which the substance is finally divided. Most colloids which disperse in organic solvents do so in a large number of them, *e.g.* rubber, which forms sols in hydrocarbons as well as in their chlorine substitution products, such as carbon tetrachloride or tetrachlorethane. The amount of solvent taken in during swelling, which precedes dispersion, can be measured if the rubber is enclosed in a vessel with

walls permeable to the solvent and impermeable to rubber. Experiments of this kind have been carried out by Posnjak,[27] who found that rubber swelled considerably more in the solvents containing chlorine than in the simple hydrocarbons. Kirchof [28] found parallelism between the degree of swelling and the viscosity of the sols; *i.e.* the solvents which caused more swelling produced the more viscous sols at equal concentrations, which is qualitatively in agreement with the view that high viscosity is due to high solvation. Whitby [29] concludes from the amounts absorbed in swelling that solvation factors as high as 40 are quite probable in rubber sols.

Liepatoff [30] has approached this problem in another way. He studies sols of a dye (geranin) in water and water-alcohol which, in appropriate concentrations, set to a jelly. This jelly undergoes syneresis (contraction with exudation of liquid), the quantity of liquid increasing as the concentration of dye decreases. The amount of water retained by the dye when syneresis ceases Liepatoff considers as water of hydration in the sense in which the term is used here; the ratio water/dye is fairly constant for different initial concentrations, and in the mean amounts to 46 c.c. of water per grm. of dye. The hydration factor calculated by applying Hatschek's equation to the results of viscosity measurements is 55, which is of the right order. More exact comparison is difficult, as impure dye was used, and the presence of salts affects the viscosity more than the syneresis.

The Anomaly of Colloidal Solutions.   In view of the failure of all concentration or ratio functions so far tried to represent the viscosity of true solutions or homogeneous liquid mixtures, the attempts to find concentration functions for disperse systems, in which the volume relations are largely a matter of conjecture, do not appear very hopeful. It is even doubtful what meaning can be attached to such functions, in view of the anomalous behaviour of such systems, which has been mentioned at the beginning of this chapter and must now be discussed more fully.

Such anomalous behaviour in colloidal solutions was first observed by Garrett [31] and A. du Pré Denning,[32] who investigated a number of sols by the oscillating disc method.

The viscosity coefficients thus determined were found to vary with the amplitude of the oscillation, being lower with high amplitudes, *i.e.* with higher angular velocity or velocity gradient; they were also found to vary systematically during the course of an experiment, and differed from values determined by the capillary method. The conditions in this method of measurement are too complicated to permit a simple interpretation. From 1906 onwards W. R. Hess [33] investigated blood, serum and several sols in a capillary instrument designed by him, in which the relative volumes discharged at different pressures are measured, and found that the volume did not increase in linear ratio with the pressure, but *more rapidly*, these liquids behaving as if the viscosity decreased with increasing pressure. In 1913 Hatschek [34] investigated gelatin sols in the concentric cylinder apparatus, and found that the angular deflection of the inner cylinder did not increase in linear ratio with the angular velocity, but more slowly; in other words, the sols again behaved as if the viscosity decreased with increasing angular velocity. The comparable variable in the two methods of measurement is of course the velocity gradient, and the anomaly of the sols may be described by saying that the viscosity apparently decreases with increasing velocity gradient. Hatschek and Edith Humphrey [35] demonstrated a few years later that this phenomenon was not confined to gelatinising sols, but was equally marked in a suspension of rigid particles in an indifferent liquid—a result confirmed again for suspensions up to 8 per cent. concentration by Hatschek and Jane [36] (concentric cylinder apparatus), and up to 25 per cent. by Köhler.[37] The concentric cylinder apparatus and the Hess viscometer were afterwards used by Freundlich and his pupils in numerous series of measurements on different sols; while Wo. Ostwald and his pupils [38] carried out a large number of investigations by means of instruments of the general design of that shown in fig. 5 (p. 26). In these the pressure varies continuously as the instrument empties, and by taking the times when the level in the graduated tubes has fallen through equal intervals, functions connecting pressure with flow in unit time,

or mean velocity and flow, can be plotted, examples of which are given in fig. 81.

A very large amount of work has been done by Bingham and collaborators, as well as by other American investigators,[39] on various systems exhibiting anomalous flow, many of which, like paints, are not colloidal solutions, and may not even form a continuous transition to them. Before the conclusions drawn from these investigations are discussed, it may be
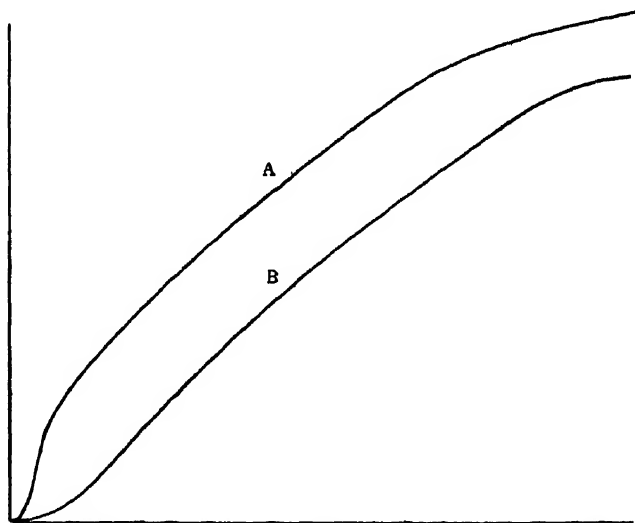
FIG. 81.—Graphs obtained with Ostwald and Auerbach's viscometer Ord. mean velocity of flow. Absc. pressure. A, 2·5 per cent mercury sulphosalicylate sol ; B, 1 per cent. gelatin sol.

advisable to give experimental results on sols and suspensions free from any implications. Fig. 82 shows results obtained in the concentric cylinder apparatus on A, a 0·5 per cent. gelatin sol, 72 hours old, at 15·5°; B, a suspension containing 6 per cent. by volume of rice starch grains in a mixture of viscous paraffin and carbon tetrachloride of the same density; and C, the latter mixture alone, both at 16°. The ordinates are deflections of the inner cylinder, the abscissæ angular velocities of the outer cylinder. C is a straight line passing through the origin, as theory requires; A and B are slightly concave to the velocity axis, but there is no doubt that they pass through the origin. (A is not comparable,

for absolute values, with B and C, as different wires were used.)

Fig. 83 shows results obtained by Herschel and Bulkley [40] on rubber sols of various concentration in a Bingham variable pressure viscometer; the ordinates are volumes passed in unit time, the abscissæ pressures in grm./cm.[2]. For normal liquids such graphs are straight lines passing through the origin, whereas those of the rubber sols are convex to the pressure axis; i.e. the volume discharged in unit time increases more rapidly than the pressure, or the apparent viscosity decreases. The curves, however, all start at the origin, just as do the angular velocity-deflection curves found with the concentric cylinder apparatus, and the same thing holds good for a large number of similar graphs of colloidal solutions in the literature.

The point is of some importance as bearing on the question whether a resistance to flow, which, unlike that of normal liquids, is a function
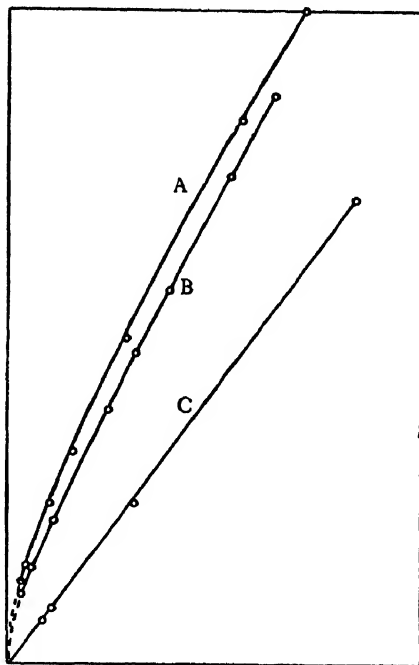
FIG. 82.—Deflection-angular velocity curves obtained with concentric cylinder apparatus (Hatschek). A, 0·5 per cent gelatin sol; B, rice starch suspension; C, paraffin+CCl$_4$.

of the velocity gradient, may be called, or treated as, a viscosity at all. The principal characteristic of viscous flow, and one apart from the constancy of the viscosity coefficient, is that the slightest shear causes flow. Bingham takes the view that the flow of a number of suspensions of high concentration, like oil paints, with which we are not concerned, but also that of many sols, is not viscous but " plastic "; flow does not begin until a certain shearing stress has been exceeded. This is, up to a point, in accordance with

Maxwell's distinction between the two types of flow: " If the form of the body is found to be permanently altered when the stress exceeds a certain value, the body is said to be soft or plastic, and the state of the body when the alteration is just going to take place is called the limit of perfect
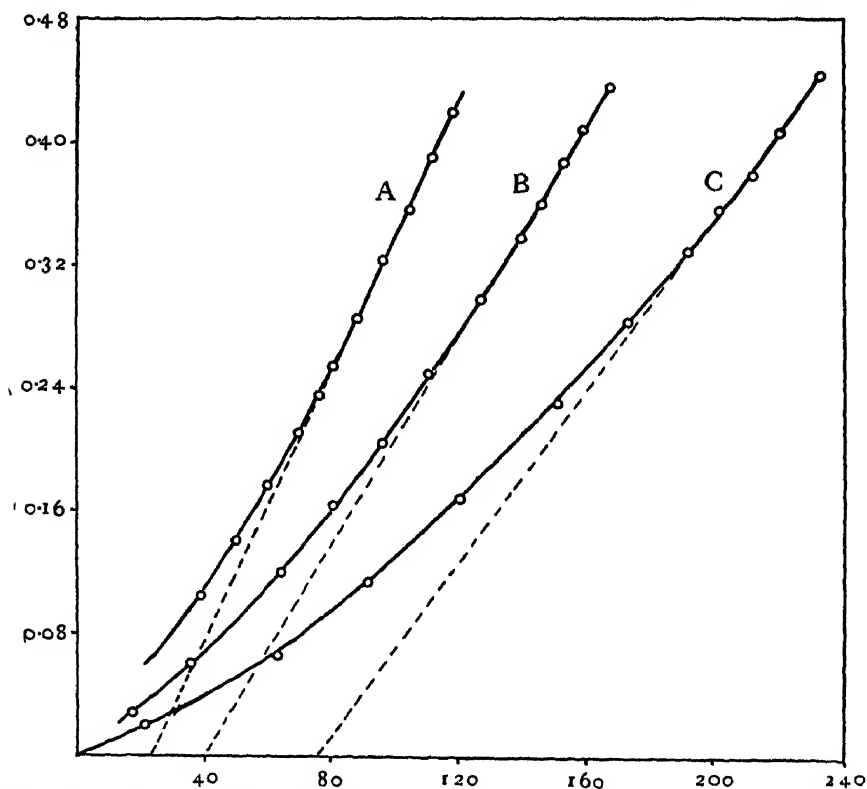
FIG. 83.—Flow-pressure graphs of rubber sols (Herschel and Bulkley). A, 0·800 per cent. ; B, 0·993 per cent.; C, 1·210 per cent.   Absc. grm. per cm.². Ord. c.c. per second.

elasticity. If the stress, when it is maintained constant, causes a strain or displacement which increases continually with the time, the substance is said to be viscous."

Herschel, who quotes this passage in one of the discussions on Bingham's work,[41] points out that Bingham does not use " the limit of perfect elasticity " as criterion when flow begins. Nor would this be possible, as many of the systems exhibiting anomalous viscosity, like the starch suspensions, cannot be

shown to possess rigidity, the kind of elasticity here in question, even by refined methods, to be briefly described later. Even with sols which, like those of gelatin, have measurable rigidity, the " limit of perfect elasticity " seems, as will be shown, very difficult to define. Bingham postulates a " yield value," *i.e.* a minimum shearing stress per unit area, below which no flow occurs, and a linear relation between flow and pressure (in a capillary) when this " yield value " is exceeded, so that the flow-pressure diagram has the form shown in fig. 84, in which the intercept OA is the pressure which produces the yield value of shearing stress.

This diagram is a purely *a priori* one, and has hardly been realised experimentally even in such paste-like systems as Bingham investigates, nor certainly in any typical sol of which the author is aware. Bingham's graphs very generally have the shape shown in dotted line; *i.e.* flow takes place at values of the shearing stress lower than the yield value. Although this is quite irreconcilable with its definition, the yield value is still assumed to be given by the intercept of " the straight portion of the curve " with the pressure axis.

Fig. 84.—Ideal plastic flow-pressure graph (Bingham).

Apart from the lack of a physical meaning in this construction, it can hardly be accepted even as a geometrical method of finding a constant in possible empirical equations for the following reason: either the curve does not actually become a straight line, in which case the choice of the " straight portion " is arbitrary and a matter of scale, or else the curve at some point literally becomes a straight line, which means a discontinuity or change in the type of flow, as has been pointed out by Breyer [42] in a discussion of Bingham and Green's results.

In Herschel and Bulkley's graph (fig. 83) the straight portions of the curves and their intercepts on the pressure axis are indicated. As flow takes place at pressures lower than those corresponding to them, and quite evidently begins as soon as the pressure exceeds zero, these intercepts, whatever their meaning, do not define yield values.

Bingham ascribes the flow at pressures lower than the yield value to " seepage," which is presumably segregation of the phases; the obvious way to avoid this disturbing factor is to use a concentric cylinder apparatus in which no escape of liquid can occur. Farrow, Lowe and Neale,[43] who have quite recently studied starch sols in both the capillary and the concentric cylinder apparatus (see below), again fail to find evidence of a yield point in either instrument.

On these grounds the author sees no reason for calling the variable resistance to shear exhibited by colloidal solutions " plasticity," or by the alternative name " consistency." Neither of these terms has been adopted by workers in Europe so far; Ostwald and his school speak simply of " viscosity," but go to the opposite extreme of applying this term even to the resistance in the region of turbulent flow. Freundlich and his school, more particularly Szegvari,[44] distinguish between a viscosity coefficient in normal liquids and a " Widerstandsgrösse " or coefficient of resistance in sols, i.e. a quantity calculated from the equations of the particular apparatus in the same way as the viscosity of a normal liquid. These resistance factors or apparent viscosities invariably decrease with increasing pressure (in the capillary) or increasing angular velocity (concentric cylinder apparatus), as the curves in figs. 81, 82 and 83 show.

These resistance factors of course define the behaviour of the sol in the given instrument only, and are not constants which permit, e.g., the calculation of the volume discharged in unit time in another instrument. As they vary with the velocity gradient, it is obvious that the behaviour of the liquid cannot be defined by equations containing a single coefficient, and this, quite apart from assumptions about the nature of the flow, is given as a reason why the term viscosity —even qualified by " variable " or " apparent "—should not be used for these anomalous liquids.

The author cannot see the cogency of this reasoning. There is nothing in the concept of viscous flow as defined, for instance, by Maxwell, which excludes a variation with the velocity gradient, although in the limiting case of normal liquids this variation is almost certainly nil. Possibly a new name may

be desirable, but the author does not feel competent to propose one. As far as any formal mathematical treatment is concerned, the attitude taken by Porter [45] seems to him perfectly adequate: "There is no fundamental reason why it (the viscosity coefficient) should be a constant. Nearly all physical factors (such as thermal conductivity, elastic constants, etc.) are found, in the long run, to be variables. It is apparently insufficient, in general, to take the viscous force per unit area as being a constant $\times dv/dr$, and some other more complicated function of the rate of shear must be assumed."

Viscosity as a Function of Velocity Gradient. That the coefficient has to be defined by reference to the velocity gradient (however inconvenient this variable) is obvious, and is quite distinct from any question of nomenclature. So far there has been no attempt to determine experimentally the velocity at any point in a sol which is being sheared, though such an investigation seems quite feasible. If in the fundamental equation of, *e.g.*, the capillary,

$$\frac{dv}{dr} = -\frac{rp}{2l\eta},$$

η is a function of dv/dr instead of a constant, v will of course be a function of r different from the parabola found for constant η. If the velocity distribution in an anomalous liquid could be determined experimentally, it would therefore be possible to find the function connecting η and dv/dr by working backwards from the velocity curve.

Failing this, which is probably the only way to a complete solution of the problem, two ways of treating it are open. One is to find empirical equations which will express the flow through a capillary, or the deflection in the cylinder apparatus, as a function of the dimensions of the apparatus and such constants characteristic of the liquid as may be necessary; the other is to assume a function $\eta = F(dv/dr)$, to introduce it into the differential equation of the apparatus, and to test the equation obtained by integration experimentally. Both these methods have already been tried.

Various Formulæ. A formula which is the mathematical

expression of fig. 84 has been put forward by Bingham [46] for the flow in a capillary:

$$Q/t = k(P + p) \quad . \qquad . \qquad . \qquad . \qquad (8)$$

where k is a constant and p also a constant, with the dimensions of a pressure, *i.e.* the pressure required in a given instrument to produce the yield value of shearing stress. The equation is that of a straight line, but, as has already been mentioned, no experimental results corresponding to it have been obtained; the Q-P curves at low pressures always curve towards the origin. Experiments on starch pastes and sols lead to the conclusion that " the lower end of the graphs must be disregarded " if a yield value is to be deduced (Herschel and Bergquist), or that " other mathematical equations " will have to be found (Porst and Moskowitz, *loc. cit.*[39]).

An equation of the form

$$Q/t = kP^n \quad . \qquad . \qquad . \qquad . \qquad (9)$$

has been proposed by Farrow,[47] de Waele,[48] and Wo. Ostwald [49] for representing the flow in the capillary; it has been applied to a considerable number of experimental data by the last-named author, with fairly good agreement. The equation again gives the relation between volume discharged in unit time and pressure for a given instrument, *i.e.* the constants k and n are not constants of the sol. Ostwald finds that an analogous equation holds for the concentric cylinder apparatus:

$$\psi = k\Omega^n,$$

where ψ is the angular deflection of the inner cylinder and Ω the angular velocity.

Herschel and Bulkley (*loc. cit.*, p. 207) propose a somewhat similar equation for representing their results with rubber sols in benzene:

$$\frac{d^4(P - K)^n}{lq} = I \quad . \qquad . \qquad . \qquad . \qquad (10)$$

where d and l are respectively the diameter and length of the capillary, q the volume discharged in unit time, while K, I,

and n are constants. Of these, n and I are constants of the material, which increase with concentration; K is too small to be detected at the concentrations used, as is evident from the nature of the curves, which pass through the origin.

As regards attempts to deduce equations for the capillary or the concentric cylinder apparatus by assuming some relation—other than simple proportionality—between the shearing stress and the velocity gradient, the first of these appears to have been made by Buckingham,[50] who adopts Bingham's assumption, but introduces it in the differential equation of flow. If F is the shear per unit area, the equation for a normal liquid (*cf.* p. 5) is

$$\eta \frac{dv}{dy} = F.$$

Buckingham assumes that no displacement occurs until a certain minimum shear per unit area f is exceeded, so that the equation becomes:

$$\eta \frac{dv}{dy} = F - f \quad . \qquad . \qquad . \qquad . \quad (11)$$

The differential equation for the velocity of flow in the capillary now becomes:

$$-\frac{dv}{dr} = \frac{1}{\eta} \left(\frac{pr}{2l} - f \right).$$

Ex hypothesi there is no shear for $pr/2l < f$, hence the material inside a radius $r_0 = 2lf/p$ moves as a solid cylinder.

If this equation is treated like that for the normal liquid (p. 17), integration gives the value of v at any radius r:

$$v = \frac{1}{\eta} \frac{p}{4l} \left[(R^2 - r^2) - f(R - r) \right],$$

and by introducing the value for r_0 the velocity of the central cylinder is found:

$$v_0 = \frac{1}{\eta} \left(\frac{pR^2}{4l} + \frac{lf^2}{P} - fR \right).$$

The velocity is constant and $= v_0$ from the centre to $r = r_0$.

The volume discharged in unit time is accordingly

$$\frac{Q}{t} = \pi r_0{}^2 v_0 + \int_{r_0}^{R} 2\pi r v dr.$$

Introducing the values for r_0 and v_0 and integrating, we obtain

$$\frac{Q}{t} = \frac{\pi R^4 p}{8\eta l}\left(1 - \frac{8lf}{3pR} + \frac{16l^4 f^4}{3p^4 R^4}\right) \qquad . \qquad . \quad (12)$$

The volume discharged is therefore smaller than it would be if the liquid were normal, but with increasing pressure increases more rapidly than the pressure, which is in agreement with experimental results.

The assumption that flow begins only when a certain shearing stress has been exceeded was again made by Szegvari and has been adopted by Freundlich.[51] Szegvari, however, simply introduced the appropriate expression into the equation connecting the moment in the concentric cylinder apparatus with the angular velocity, which is tantamount to assuming that the velocity gradient is uniform. The assumption is not correct even for normal liquids, and with abnormal ones evades the whole problem. The correct procedure, as in the case of the capillary, is to introduce the expression for the shear into the differential equation, which thus becomes:

$$M = 2\pi r^2 l\left(\theta + \eta r \frac{d\omega}{dr}\right) \qquad . \qquad . \qquad . \quad (13)$$

where θ is a constant analogous to the f in Buckingham's equation. Reiner and Riwlin,[52] who treated the concentric cylinder problem, call it " Fliessfestigkeit," $i.e.$ it has the character of an ultimate shearing strength; before the stress reaches this value, the liquid adhering to the outer cylinder moves as a whole, just as it moves like a solid cylinder in the axial portion of the capillary. When the stress exceeds θ everywhere in the liquid, the integral of equation (13), with the same boundary conditions as for a normal liquid, gives the moment for the abnormal liquid:

$$M = \frac{4\pi R_1{}^2 R_2{}^2 l\eta}{R_2{}^2 - R_1{}^2}\Omega + \frac{\theta}{\eta}\log_e\frac{R_2}{R_1} \qquad . \qquad . \quad (14)$$

It is easy to see that the moment increases less rapidly than the angular velocity, which is in accordance with experience. The formula has never been tested; in an earlier paper Reiner,[53] in ignorance of Buckingham's paper, treated the problem of the capillary and obtained the same result as given in equation (12). He tested it on a single set of experimental results by Freundlich and Schalek [54] with fair agreement.

The assumption made in the deductions just described, that a certain shearing stress must be exceeded before flow begins, seems at first sight to be supported by the fact, which has been demonstrated experimentally, that a number of sols can support small shearing stresses for a short time, *i.e.* possess measurable moduli of rigidity. Whether these are identical with, or even of the same order as, the f or θ in Buckingham's and Reiner's equations it is impossible to say from the available data. These constants as well as η would have to be calculated from measurements made on the same sol in different instruments before it was possible to say that they were true constants of the sol and independent of the dimensions of the particular apparatus used

Even if the proved rigidity of such sols as, *e.g.*, those of gelatin should be found to account quantitatively for their variable viscosity, this explanation fails for suspensions of rigid particles, where rigidity has never been demonstrated and seems extremely improbable. The only attempt to treat such systems mathematically has been made by Reiner and Riwlin,[55] who start from a suggestion made by Hatschek [56] that the particles carry with them liquid envelopes which have a maximum volume when the liquid is at rest, and are sheared off increasingly with increasing velocity gradient. As a basis for mathematical formulation Reiner and Riwlin make two assumptions: (1) that for suspensions of particles with constant radius Einstein's linear equation (*cf.* p. 196) holds, and (2) that the virtual volume of the particles f (volume of particle + volume of liquid envelope) with increasing velocity gradient G decreases exponentially between two limiting values f_0 when the liquid is at rest, and f_∞ when the gradient is infinitely high:

$$f = (f_0 - f_\infty)e^{-cG} + f_\infty \qquad . \qquad . \qquad . \quad (15)$$

When this value for the variable volume is introduced in the Einstein formula it becomes:

$$\eta' = \eta[1 + 2\cdot5(f_0 - f_\infty)e^{-cG} + 2\cdot5f_\infty] \quad . \quad . \quad (16)$$

This expression is introduced in the differential equations for the concentric cylinders or the capillary, and the velocity gradient G expressed as $r\,d\omega/dr$ or dv/dr. The integrations cannot be carried out in closed form, but expansion in series is practicable. The final equations obtained for the " resistance coefficient " or apparent viscosity are—

For the concentric cylinders:

$$w = (\eta_0 - \eta_\infty) \exp\left(-c\frac{R_1{}^2 + R_2{}^2}{R_2{}^2 - R_1{}^2}\Omega\right) - \eta_\infty \quad . \quad (17)$$

For the capillary:

$$w = (\eta_0 - \eta_\infty) \exp\left(-\frac{2cRp}{\eta_0 l}\right) + \eta_\infty \quad . \quad . \quad (18)$$

where η_0 and η_∞ are two constants, viz. the viscosity at rest and the viscosity at infinitely high velocity gradient, and c is a third constant, which defines the rate of decrease of the virtual volume with increasing velocity gradient.

The equations (17) and (18) have not been tested on experimental figures so far, but exponential equations with three constants should be capable of being fitted to the comparatively simple w-p or w-ω curves. The deduction, however, assumes that, for constant volume of particles the linear Einstein formula holds, while all the experimental evidence available so far shows that it fails at very moderate concentrations. The deviation from a linear law may, of course, be in part due to the unsuspected variation with velocity gradient itself, for which no allowance had been made in the older investigations; but the formula seems an insecure foundation on which to base a very difficult mathematical treatment. Until the equations have been tested on the same sol with different instruments, it is impossible to decide whether the assumptions made in deducing them can be accepted.

The only attempt to express the results of viscosity measurements made in different apparatus in terms of shear-

ing stress and velocity gradient, *i.e.* in a way which permits direct comparison of such results and a decision whether the constants used are constants of the liquid free from apparatus constants, has been made quite recently by Farrow, Lowe and Neale.[57] They assume that, instead of the linear relation between shearing stress and velocity gradient, which holds good for normal liquids, the following applies to sols:—

$$F^N = \eta' \frac{dv}{dy} \quad . \qquad . \qquad . \qquad . \qquad (19)$$

in which N and η' are constants of the liquid. The same assumption, expressed slightly differently, was made by Porter [58] about the same time. He assumes a variable viscosity η which is a function of the velocity gradient:

$$\eta = \eta' \left(\frac{dv}{dy}\right)^{-n} \qquad . \qquad . \qquad . \qquad (20)$$

The shearing stress per unit area on this assumption becomes:

$$F = \eta' \left(\frac{dv}{dy}\right)^{1-n},$$

which, assuming η' to be the same in both equations, agrees with Farrow's assumption when $1/N = 1 - n$.

By introducing this value for the shearing stress into the differential equation of the capillary, Porter and Farrow obtain the same expression for the volume discharged in unit time, which, using Farrow's symbols, is

$$\frac{Q}{t} = \left(\frac{p}{l}\right)^N \frac{\pi R^{N+3}}{(N+3)2^N} \frac{1}{\eta'} \quad . \qquad . \qquad . \qquad (21)$$

and becomes Poiseuille's equation for $N = 1$.

Porter tested the equation on sols of soluble starch containing 6, 8, and 10 per cent., and found good agreement.

Farrow writes equation (21) as follows:—

$$\left(\frac{pR}{2l}\right)^N = \eta' \frac{Q(N+3)}{t\pi R^3}.$$

Since $pR/2l$ is the shearing stress at the wall when stationary flow is established, it follows from (19) that the velocity gradient at the wall is

$$\frac{dv}{dr} = \frac{Q(N+3)}{t\pi R^3} \qquad . \qquad . \qquad . \quad (22)$$

It is possible thus to express the results of measurements in capillary tubes in terms of shearing stress and maximum velocity gradient, and to make them independent, not only of the dimensions, but of the type of instrument used. They can then be compared with the results of measurements in the concentric cylinder apparatus, and if N and η' are real constants of the liquid, they must satisfy the equations to be found for this apparatus.

By introducing the expression (19) for the shearing stress into the differential equation of the concentric cylinders, we obtain:

$$\left(\frac{M}{2\pi R_1^2 L}\right) = 2N\Omega\eta' \frac{R_2^{2N}}{R_2^{2N} - R_1^{2N}} \qquad . \qquad . \quad (23)$$

in which all the symbols have the usual meaning. From simple static considerations it follows that the term in brackets is the shearing stress per unit area on the inner cylinder, and that therefore the velocity gradient at this surface is

$$2N\Omega \frac{R_2^{2N}}{R_2^{2N} - R_1^{2N}} \qquad . \qquad . \qquad . \quad (24)$$

If the inner cylinder is suspended by a wire of torque per unit twist τ, $M = \phi\tau$, where ϕ is the deflection of the inner cylinder.

Measurements on the same sols (starch pastes containing formaldehyde, which prevents setting and retards the spontaneous change of viscosity) were made both in capillaries and in a concentric cylinder apparatus, and the shearing stresses at the wall of the capillary or the surface of the inner cylinder calculated from the equations just given, as well as the velocity gradients at these surfaces. Approximate values of N were first obtained by plotting log P against log $1/t$ (capillary), or log M against log $1/\Omega$.

Examination of the results, which it is not necessary to give *in extenso*, shows that neither N nor η' is a constant of the material at concentrations higher than 1 per cent. The values for 1 per cent. sols show reasonably good agreement. They are:

From measurements in concentric cylinder apparatus—
   N =1·04, mean value of η' =0·0373, maximum deviation 6 per cent. of mean value.
From measurements in capillary viscometer—
   N =1·11, mean value of η' =0·0353, maximum deviation 1·1 per cent. of mean value.

The 2 per cent. sol already shows much greater discrepancies:

From measurements in concentric cylinder apparatus—
   N =1·46, mean value of η' =3·19, maximum deviation 16·3 per cent. of mean value.
From measurements in capillary viscometer—
   N =1·40, mean value of η' =2·16, maximum deviation 2·8 per cent. of mean value.

For higher concentrations the discrepancies between the values deduced with the two types of apparatus become very much greater.

Farrow gives two graphs (figs. 85 and 86), in the first of which the velocity gradients are plotted against the shearing stresses, and in the second the logarithms of these quantities. The following gives the essential points of Farrow's own discussion of the results:—

The fact that the experimental points for any one paste lie on a smooth curve shows that the method of expression used has succeeded in correlating the results of flow measurements made in viscometers of differing types and dimensions, over a total range of velocity gradient of 300,000-fold. It therefore seems possible to measure the flow of anomalous liquids in capillary instruments, and to express their condition at a given velocity gradient in terms of the constants of a simple equation (19) independently of the dimensions of the instrument.

Over a range which is comparatively small compared with the total range of measurement, the log velocity gradient-log

stress points lie on a straight line. It is therefore probable
that the assumption represented by equation (19) holds
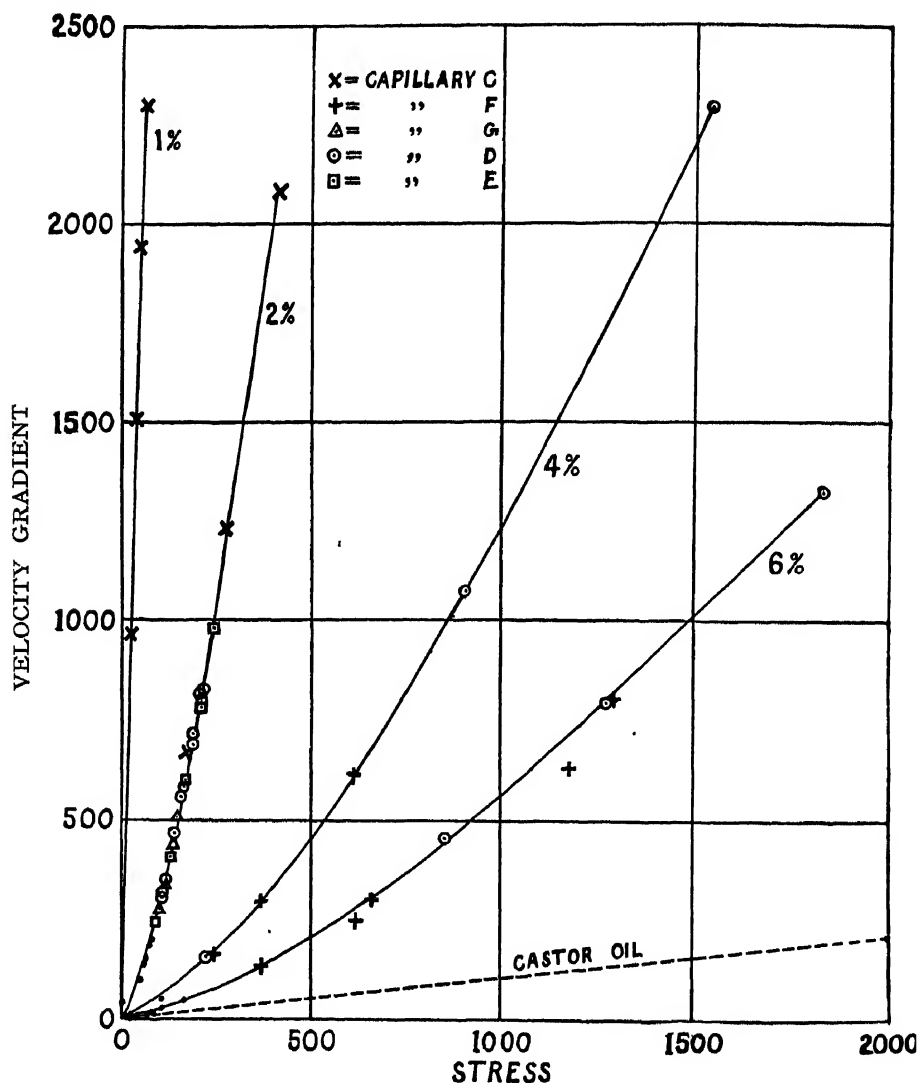
FIG. 85.—Stress-velocity gradient graphs of starch pastes in different
capillaries (Farrow, Lowe and Neale).

approximately over a limited range, and that therefore the
method of calculating velocity gradients at particular regions
from total flow is a close approximation.

Over a wide range the lines relating log stress and log
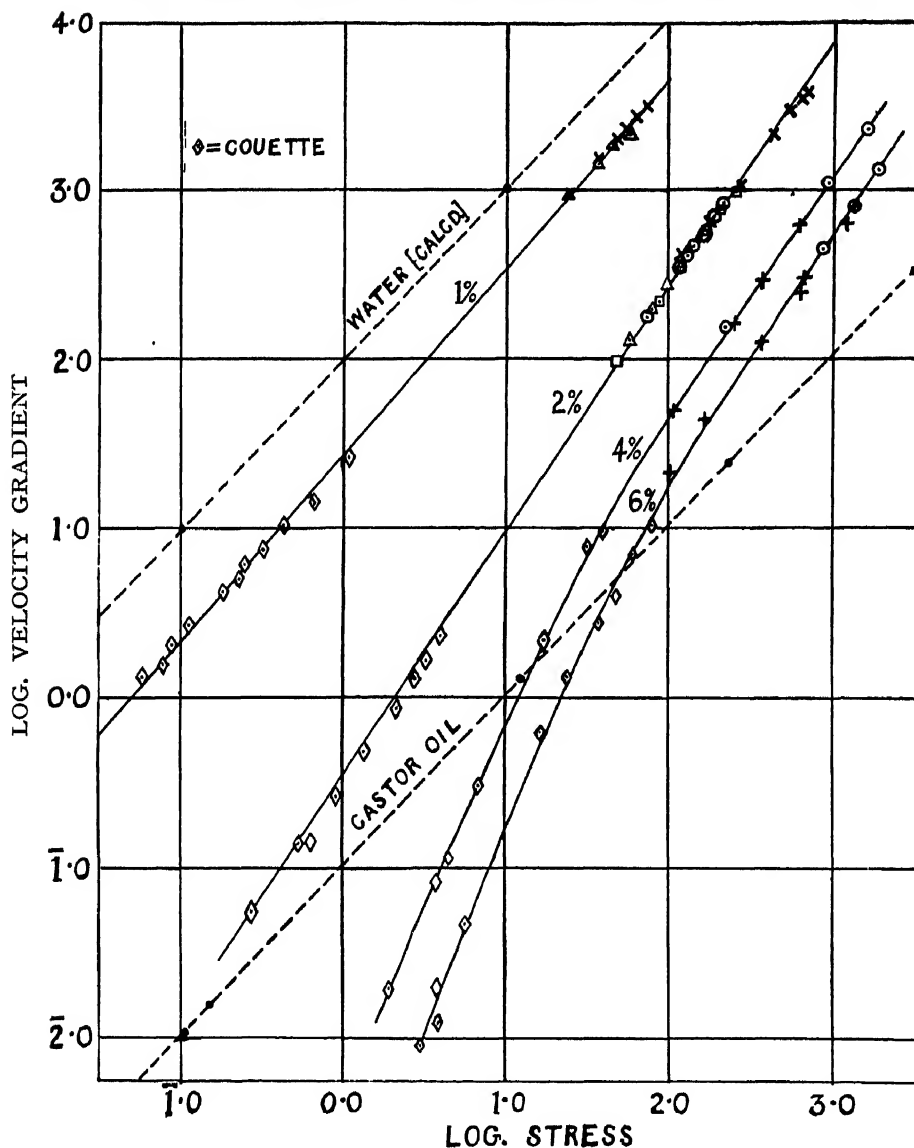
FIG 86 —Log stress-log velocity gradient graphs of starch pastes in capillaries and Couette (concentric cylinder) apparatus (Farrow, Lowe and Neale).

velocity gradient, which should be straight if equation (19) is valid, appear to have a slight curvature, which is the

greater the more viscous the liquid. In other words, N, the slope of the log-log line, is constant over a small range only, and increases very slowly for the more viscous liquids as the velocity gradient decreases. On this account different values for N, and therefore for η', are given by the same liquid in the capillary viscometer, where the gradient is high, and in the concentric cylinder apparatus, where it is low. It appears, therefore, that the original assumption is useful chiefly as a means of eliminating instrument dimensions and of obtaining values of pure shearing stress and velocity gradient in the liquid to a close approximation. It is, of course, not possible to calculate exact values of velocity gradient until an exact relation between it and shearing stress is found, and since such a relation must itself depend on viscometer measurements, the only method of progress is by successive approximations. This, however, is quite practicable, since, particularly in the concentric cylinder apparatus, change of the stress-velocity gradient relation usually involves only a second order correction to the velocity gradient calculated.

Farrow, Lowe and Neale add, what is indeed evident from the graphs, that they find no evidence of any " yield value."

A point deserving mention is that the graphs do not give any direct evidence of the inconstancy of η', which is considerable at the higher concentrations.

Although the method developed by these authors is only, as they say, a first approximation, it is without doubt an important step towards the rational aim of co-ordinating the real variables, shearing stress and velocity gradient, instead of developing merely empirical relations for given instruments. If the direct determination of the velocity distribution, to which reference has been made, should prove impracticable, more complicated functions than that tested by Farrow will have to be tried in the same way.

Maxwell's Theory of Viscosity. As has been mentioned before, many sols possess measurable rigidity, and this opens up one more theoretical possibility of arriving at a method for finding their true viscosity. A connection between elastic modulus and viscosity coefficient has been formulated by

Maxwell [59] as follows: a strain or deformation of some kind S is produced in a body (about the structure or state of aggregation of which no assumptions are made); a state of stress or elastic force F is thus excited, and the relation between stress and strain may be written: $F = ES$, where E is the modulus of elasticity for the particular kind of strain. In a body free from viscosity F will remain $= ES$, and

$$\frac{d\mathrm{F}}{dt} = \mathrm{E}\frac{d\mathrm{S}}{dt} \quad . \qquad . \qquad . \qquad . \quad (25)$$

If, however, the body is viscous, the stress F will not remain constant, but will tend to disappear at a rate depending on F and on the nature of the body. The simplest assumption is that this rate of disappearance is proportional to the stress, and the equation may then be written:

$$\frac{d\mathrm{F}}{dt} = \mathrm{E}\frac{d\mathrm{S}}{dt} - \frac{\mathrm{F}}{\mathrm{T}}. \quad . \qquad . \qquad . \quad (26)$$

If S is assumed to be constant, integration gives the equation

$$\mathrm{F} = \mathrm{E}Se^{-t/\mathrm{T}} \quad . \qquad . \qquad . \qquad . \quad (27)$$

where T is an integration constant with the dimensions of a time. For $t = \mathrm{T}$ the stress F has decreased to $1/e$ of its initial value. When $t = \infty$, the body has lost all internal stress.

If S is variable, the most interesting case is that when $d\mathrm{S}/dt$ is constant, *i.e.* there is steady motion which continually increases the displacement. Integration of equation (26) gives:

$$\mathrm{F} = \mathrm{E}\mathrm{T}\frac{d\mathrm{S}}{dt} + \mathrm{C}e^{-t/\mathrm{T}} \quad . \qquad . \qquad . \quad (28)$$

C is an integration constant. The equation shows that F tends to a constant value as the second term on the right tends to zero with increasing t. Maxwell concludes: " The quantity ET, by which the rate of displacement must be multiplied to get the force, may be called the coefficient of viscosity. It is the product of the coefficient of elasticity E and a time T, which may be called ' the time of relaxation ' of the elastic force. In mobile fluids T is a very small fraction

of a second, and E is not easily determined experimentally. In viscous solids T may be several hours or days, and then E is easily measured. *It is possible that in some bodies* T *may be a function of* F." (My italics.—E. H.)

This means that, for a body possessing both rigidity and viscosity, the simple relation should hold:

$$\eta = ET \quad . \quad . \quad . \quad . \quad (29)$$

E being the modulus of rigidity, and T the "relaxation time," as defined above.

It therefore would appear possible to find the real viscosity coefficient of a material possessing rigidity (" the particular kind of strain " in question being a shear) by determining the modulus and the time of relaxation; the first step being to verify whether the law of relaxation is that assumed by Maxwell. This can be done by maintaining a certain deformation S constant and determining at intervals the stress F required to maintain it; if equation (27) holds, the F-*t* curve must be a logarithmic line. We have already described one investigation of the kind, that of Trouton and Andrews (p. 187), on pitch, in which the relaxation curve was found not to be logarithmic. Similar determinations of the relaxation-time curve, as well as of the modulus, have been carried out with a number of colloidal solutions, and may be briefly described here.

Rigidity in Colloidal Solutions. The first investigator to determine the modulus of rigidity and the relaxation of sols (a single gelatin sol was examined) was Schwedoff.[60] A cylinder is suspended from a long wire coaxially in a cylindrical vessel containing the liquid to be investigated. The upper end of the wire is twisted through an angle ϕ; if the liquid is simply viscous, the cylinder follows the wire with a decreasing velocity until it has moved through the angle ϕ, *i.e.* until no torsion is left in the wire. If, however, the liquid also possesses rigidity, the cylinder does not follow, but rotates through an angle $\omega(<\phi)$ only, and maintains this position for a short time, the elastic deformation in the liquid balancing the torque of the wire, which is $N(\phi - \omega) = N\delta$, N being the torsional moment of the wire for unit angle.

Mathematical treatment leads to an equation which has the same form as that for a viscous liquid between concentric cylinders:

$$E = \frac{N}{4\pi h}\left(\frac{1}{R_1{}^2} - \frac{1}{R_2{}^2}\right)\frac{\delta}{\omega} \quad . \qquad . \qquad . \quad (30)$$

where E is the modulus of rigidity of the liquid, and the other symbols have the same meaning as before; h, the effective height of the inner cylinder, must again be found by elimination.

The inner cylinder does not remain at the deflection ω, but relaxation sets in, and the cylinder gradually follows the wire. In some cases this continues until no torsion is left in the wire, while in others the liquid supports a residual deformation ($<\omega$) apparently indefinitely. The relaxation, as defined by Maxwell, *i.e.* the stress required to maintain the deformation ω, can be studied by reducing the torsion of the wire from time to time, so as to maintain the cylinder at the deflection ω, and plotting these torques, $\delta_1, \delta_2, \ldots \delta_n$ against the times $t_1, t_2, \ldots t_n$; if the simple law assumed by Maxwell holds, the δ-t curve is a logarithmic line, and the stress is $=0$ when $t=\infty$. In the sol studied by Schwedoff (0·5 per cent. gelatin), and in several of the sols examined in an apparatus similar to his by Hatschek and Jane,[61] the relaxation is, however, not of this type, but the sol apparently maintains a small residual deformation permanently. The magnitude of this permanent deformation is very uncertain, as the whole apparatus and the condition of the liquid are highly susceptible to even small vibrations. Schwedoff found that the relaxation of his sol could be expressed by the following equation—which, as he points out, differs from Maxwell's ·—

$$\delta_t = a(1 + be^{-\alpha t}) \quad . \qquad . \qquad . \quad (31)$$

in which δ_t is the torsion in the wire at the time t, and a, b, and α are constants; for $t=\infty$, $\delta_\infty = a$, which therefore is the residual deformation. The constants can be determined from three sets of values for δ and t; Hatschek and Jane have done so for one of the sols studied by them (0·3 per cent

benzo-purpurin), but found that a was far from constant even over a small range. The relaxation of this and other sols is accordingly not expressed either by Maxwell's or by Schwedoff's equation. The relaxation curve just mentioned is shown in fig. 87. As the Maxwellian relaxation time, *i.e.* the time in which the deformation decreases to $1/e$ of its initial value, is exceeded in this and other determinations, Hatschek and Jane have calculated the viscosity of such sols from the relation,

$$\eta = ET,$$

the moduli E having been determined previously. The
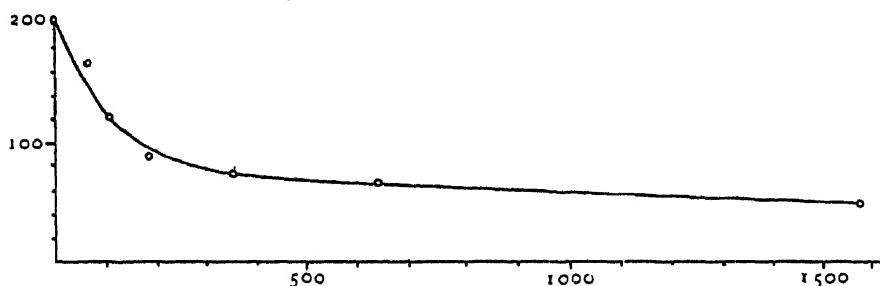
FIG. 87.—Relaxation curve of benzo-purpurin sol Absc seconds.
Ord. remaining torque in arbitrary units

viscosities thus found are of the order of 10^2 to 10^4 poises, and the order agrees quite well with that of the apparent viscosities determined directly at extremely low velocity gradients, of the order of 10^{-5} to 10^{-6} cm./sec./cm. These can hardly be the " real " viscosities, and the conclusion seems to be that the first step in attacking the problem on these lines is to find the true law of relaxation and to transform Maxwell's equation accordingly. At the moment the experimental data are hardly sufficiently numerous to afford a safe basis for this inquiry. The difficulties to be overcome are very fully discussed in a recent paper by Freundlich and Rawitzer.[62]

Anomalous Turbulence. In conclusion, a further anomaly of sols may be mentioned which may prove to be of theoretical importance—the anomalous onset of turbulence. Hatschek and Jane (*loc. cit.*,[61]) found, when investigating ammonium oleate in the concentric cylinder apparatus, that the apparent

viscosity—as in all other sols—at first decreased with increasing angular velocity, and then rose very abruptly at an angular velocity well below that at which turbulence sets in in pure water. Ostwald suggested that this apparent rise was caused by turbulence, and the correctness of the explanation was proved experimentally by Andrade and Lewis [63] in their transparent concentric cylinder apparatus, in which the type of flow is made visible by small suspended aluminium particles. Turbulence set in at an angular velocity about 3/4 of the critical velocity for water, although the viscosity of the sol, measured in an Ostwald viscometer, was somewhat higher than that of water, and its density about the same.

Ostwald [64] considers it probable that the phenomenon is not an isolated one, and questions whether, in the presence of particles or of " structures " in sols, true laminar motion occurs in colloidal solutions at all. This interesting question will be answered incidentally when, as suggested above, a method has been found of determining the velocity gradient at any point in a sol. Until this is accomplished no very substantial progress is to be expected.

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CHAPTER XIII

TECHNICAL VISCOMETERS

A NUMBER of instruments are used in the oil industry, in which the time of efflux of a definite volume through very short tubes (about 7 diameters long) is determined, and, with the name of the instrument prefixed, is used to describe the viscosity of the oil examined. The principal types are: the Redwood (British Empire), the Saybolt Universal (United States), and the Engler viscometer (Germany and other continental countries). With the last-named instrument two methods of expressing the observations are employed: either the time of efflux of the defined volume is stated (Engler seconds), or that time divided by the time of efflux of the standard volume of water (Engler degrees).

The liquid in all these instruments is discharged into the air and collected in a flask with a mark defining the standard volume. The flow does not conform to Poiseuille's Law, the times are not in any simple relation with the viscosities, nor are the Engler degrees even approximately relative viscosities. Although most of the recent works on oils [1] are strongly in favour of expressing viscosity in absolute units, the continued use of the various instruments mentioned seems to be taken for granted, as the use of correct methods is held to entail too great an expenditure of trouble and time. As regards the last point, the case against correct capillary viscometers does not seem strong; the Redwood instrument is standardised with " refined rape oil," the time of efflux for 50 c c. at 15·5° being 535 seconds. A capillary instrument with a volume of 5 c.c. and a time of efflux of 200 seconds would save time and oil, and give viscosity in absolute units.

In the meantime it has been found necessary to compare the data obtained with the three standard instruments, and to express them all in absolute units. It is obvious that comparison must be made not between viscosities, but between kinematic viscosities. This has been done by Herschel,[2] who finds that the kinematic viscosity can be expressed as a function of the time of efflux found with the technical instruments,

$$\frac{\eta}{\rho} = At - \frac{B}{t},$$

where A and B are instrument constants, which can be determined by measuring the times of flow of suitable calibrating liquids. Tables XXVII to XXX give all the data required for interconverting results obtained with any of the standard instruments, and expressing them as kinematic viscosities.

TABLE XXVII

FACTORS FOR REDUCING REDWOOD TIME TO SAYBOLT UNIVERSAL TIME OR ENGLER DEGREES (HERSCHEL)

Red-wood time in seconds	Kine-matic vis-cosity	Saybolt time. Red-wood time	Engler degrees. Red-wood time	Red-wood time in seconds	Kine-matic vis-cosity	Saybolt time Red-wood time	Engler degrees. Red-wood time.
30	0·0154	1·08	0 0365	80	0·1845	1·16	0·0349
32	0·0245	1·09	0·0363	85	0·1989	1 16	0·0349
34	0 0332	1·09	0·0361	90	0·2131	1·17	0·0348
36	0 0414	1·10	0 0360	95	0·2272	1·17	0·0348
38	0·0493	1·10	0·0359	100	0·2412	1 17	0·0348
40	0·0570	1·11	0·0358	110	0·2689	1·17	0·0347
42	0 0645	1·11	0 0357	120	0·2964	1·17	0 0347
44	0·0717	1·12	0·0357	130	0·3236	1·17	0·0347
46	0 0788	1·12	0·0356	140	0·3506	1 18	0·0347
48	0·0854	1·13	0·0355	150	0·3775	1·18	0·0347
50	0·0924	1·13	0 0354	160	0·4043	1·18	0·0346
55	0·1088	1·14	0·0354	180	0·4576	1·18	0 0346
60	0·1247	1·14	0·0353	200	0·5106	1·18	0·0346
65	0·1401	1·15	0·0352	225	0·5766	1·18	0·0346
70	0·1552	1·15	0·0351	250	0·6425	1 18	0·0345
75	0·1700	1·16	0·0350				

TABLE XXVIII

FACTORS FOR REDUCING ENGLER TIME TO SAYBOLT UNIVERSAL
TIME OR REDWOOD TIME (HERSCHEL)

Engler time in seconds.	Kinematic viscosity.	Saybolt time. / Engler time.	Redwood time. / Engler time.	Engler time in seconds.	Kinematic viscosity.	Saybolt time. / Engler time.	Redwood time. / Engler time.
56	0·0155	0·578	0·535	130	0·1624	0·641	0·557
58	0·0210	0·581	0·537	140	0·1793	0·645	0·558
60	0·0260	0·585	0·538	150	0·1956	0·649	0·559
62	0·0309	0·588	0·540	160	0·2121	0·652	0·559
64	0·0357	0·592	0·541	180	0·2438	0·654	0·560
66	0·0403	0·595	0·542	200	0·2753	0·656	0·560
68	0·0449	0·598	0·543	225	0·3140	0·658	0·561
70	0·0496	0·601	0·544	250	0·3525	0·659	0·561
75	0·0604	0·605	0·546	275	0·3904	0·660	0·562
80	0·0709	0·611	0·547	300	0·4282	0·661	0·562
85	0·0811	0·616	0·549	325	0·4660	0·662	0·563
90	0·0907	0·621	0·550	350	0·5038	0·663	0·563
95	0·1004	0·625	0·552	375	0·5413	0·664	0·564
100	0·1095	0·629	0·553	400	0·5784	0·665	0·564
110	0·1279	0·633	0·555	500	0·7271	0·666	0·565
120	0·1453	0·637	0·556	600	0·8753	0·667	0·565

TABLE XXIX

FACTORS FOR REDUCING ENGLER DEGREES TO SAYBOLT UNIVERSAL
OR REDWOOD TIME (HERSCHEL)

Engler degrees.	Kinematic viscosity.	Saybolt time. / Engler degrees	Redwood time. / Engler degrees	Engler degrees.	Kinematic viscosity	Saybolt time / Engler degrees	Redwood time / Engler degrees
1·10	0·0166	29·7	27·5	2·30	0·1416	32·8	28·5
1·15	0·0234	29·9	27·6	2·40	0·1506	32·9	28·5
1·20	0·0299	30·1	27·6	2·50	0·1593	33·0	28·5
1·25	0·0358	30·3	27·7	2·60	0·1677	33·1	28·6
1·30	0·0420	30·5	27·8	2·70	0·1764	33·2	28·6
1·35	0·0476	30·7	27·8	2·80	0·1849	33·3	28·6
1·40	0·0534	30·9	27·9	2·90	0·1935	33·4	28·6
1·45	0·0590	31·1	27·9	3·00	0·2019	33·5	28·7
1·50	0·0646	31·3	28·0	3·50	0·2432	33·6	28·7
1·60	0·0750	31·5	28·1	4·00	0·2833	33·7	28·8
1·70	0·0853	31·7	28·1	4·50	0·3228	33·9	28·8
1·80	0·0953	31·9	28·2	5·00	0·3624	33·9	28·8
1·90	0·1046	32·1	28·3	6·00	0·4404	34·0	28·9
2·00	0·1143	32·3	28·3	7·00	0·518	34·1	28·9
2·10	0·1236	32·5	28·4	8·00	0·595	34·1	28·9
2·20	0·1326	32·6	28·5	9·00	0·671	34·2	29·0

TABLE XXX

FACTORS FOR REDUCING SAYBOLT UNIVERSAL TIME TO ENGLER
DEGREES OR REDWOOD TIME (HERSCHEL)

Saybolt time in seconds.	Kinematic viscosity.	Engler degrees. / Saybolt time.	Red-wood time. / Saybolt time.	Saybolt time in seconds.	Kinematic viscosity.	Engler degrees / Saybolt time.	Red-wood time / Saybolt time.
32	0·0142	0·0337	0·928	85	0·1658	0·0305	0·862
34	0·0219	0·0334	0·920	90	0·1780	0·0304	0·860
36	0·0292	0·0332	0·914	95	0·1901	0·0303	0·858
38	0·0362	0·0330	0·909	100	0·2020	0·0302	0·856
40	0·0430	0·0328	0·905	110	0·2256	0·0301	0·855
42	0·0495	0·0326	0·901	120	0·2490	0·0300	0·854
44	0·0559	0·0324	0·897	130	0·2722	0·0299	0·853
46	0·0621	0·0322	0·893	140	0·2951	0·0299	0·852
48	0·0681	0·0319	0·889	160	0·3408	0·0298	0·851
50	0 0740	0·0317	0·885	180	0·3860	0·0297	0·850
55	0·0883	0·0315	0·881	200	0·4310	0·0296	0·849
60	0·1020	0·0313	0·871	225	0·4870	0·0295	0·848
65	0·1153	0·0312	0·873	250	0·5428	0·0294	0·847
70	0·1283	0·0310	0·870	300	0·6540	0·0293	0·847
75	0·1410	0·0308	0·867	350	0·7648	0·0293	0·846
80	0·1535	0·0307	0 865	400	0·8755	0·0292	0·846

The problem of deducing kinematic viscosities from data on flow through short tubes, to which Poiseuille's Law does not apply, has been treated analytically by Schiller.[3]

A technical concentric cylinder instrument (without guards or complete elimination of the bottom and surface effects) is the MacMichael viscometer.[4] An accuracy within 5 per cent. is stated to be obtainable with it   The author has not found records of any extended series of tests, but believes that the Bureau of Standards has not so far found it possible to express results obtained with this and other torsion instruments in absolute units.

The Michell viscometer,[5] finally, deserves mention on account of its simplicity and the novelty of the principle underlying it.   It consists of a steel ball one inch (25·4 mm.)

diameter, and a hollow spherical segment (fig. 88), which is fixed to a hollow stem serving as a thermometer pocket and carrying an ebonite handle.   Three small projections are provided on the spherical hollow and are accurately ground to project from 0·025 to 0·050 mm., so that a space of this thickness remains clear between the hollow and the ball when the latter is pressed home.   A recess about 0·4 mm. wide and deep is countersunk round the rim of the hollow.

For rough determinations at ordinary temperature a few drops of oil are placed in the hollow cup, and this is pressed down on the ball; the instrument is then lifted, and the time from the moment of lifting to the dropping of the ball taken with a stop-watch.   The time divided by the "constant" of the instrument gives the absolute viscosity.   For more accurate determination at definite temperatures or over a temperature range the whole operation, *i.e.* pressing the cup on the ball and allowing it to drop off, is carried out under the liquid, which is being maintained at the desired temperature in a suitable vessel.

FIG. 88.—
Michell viscometer.

The time taken by the ball to become detached is controlled by the rate at which the liquid flows from the annular space round the rim of the cup into the space between it and the ball.   The instrument is calibrated with suitable liquids, and the error is stated to be of the order of about 4 per cent.   An approximate theory of the instrument has been developed by Michell.[6]

[1] E. G. D. HOLDE, *Kohlenwasserstofföle und Fette*, 6th ed. (Berlin, 1924).

[2] W. H. HERSCHEL, *Bur. Stand. Technolog. Papers*, No. **100** (1918), No. **112** (1918) ; No. **210** (1922).

[3] L. SCHILLER, *Zeitsch. f. angew. Math. und Mechanik*, **2**, 96 (1922)

[4] Made by EIMER & AMEND, New York (Bulletin 280).

[5] *The Engineer* (London), **134**, 532 (1922).

[6] See *The Mechanical Properties of Fluids*, p. 119 *et seq.* (London : Blackie & Sons, Ltd., 1923).

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